Table IX. MNDO-PM3 Heats of Formation of the Molecules Pertinent to Reaction II

structure^a	ΔH_f^b (kcal/mol)
1b	119.0
2b	74.7
3b	234.1 (40.4)
3c	231.6 (37.9)
4b	173.9 (−19.8)
4c	173.4 (−20.3)

^{a} See Figure 1. ^{b} Enthalpies relative to **1b** + **2b** are listed in parentheses.

mated, and the formation of **6c** is favored over that of **6b** by 2.5 kcal/mol. We believe that this failure of the MNDO-PM3 method can be directly attributed to the absence of dispersive interactions and the resulting exaggeration of the repulsion between the phenyl rings of the reactants.

Conclusions

The experimental and theoretical data presented above allows us to conclude that Diels–Alder cycloaddition is the rate-determining step for both reactions I and II. The addition involves a quite early transition state with the activation energy estimated at about 13 kcal/mol by the theoretical methods, in good agreement with the measured activation enthalpy of ca. 16 kcal/mol. In contrast, our calculations indicate that the second steps of both reactions I and II have either a very low reaction barrier or no barrier whatsoever.

For the reaction II, the formation of 3,4-diphenylpyridazine is preferred over that of 3,5-diphenylpyridazine by the estimated difference in the activation energies of 4.0 kcal/mol. The regiospecificity of reaction II cannot be predicted correctly at the HF level. However, the MP2 calculations provide the right answer, as they include the attractive dispersion interactions between the phenyl rings of the reactants, which are neglected at the Hartree–Fock level of theory. Surprisingly, the regiospecificity of reaction II is controlled primarily by the dispersion interactions, where out of the 4.0 kcal/mol difference in $\Delta E^{\ddagger}$, an estimated 2.7 kcal/mol comes from the purely electronic effects, −3.6 kcal/mol from steric repulsions, and 4.9 kcal/mol from the dispersive attraction between the phenyl rings.

The semiempirical MNDO-PM3 method is incapable of predicting either the activation energy or the regiospecificity of reaction II correctly. We believe that, by documenting the importance of including the attractive dispersion interactions in calculations aimed at prediction of rates and specificities of cycloadditions, an issue which has been mostly neglected in the chemical literature, the aforedescribed research will contribute to better understanding of the factors that influence these reactions.

Acknowledgment. This work was partially supported by the Deutsche Forschungsgemeinschaft (DFG), Fonds der Chemischen Industrie, the National Science Foundation under Contract CHE-9015566, the Camille and Henry Dreyfus Foundation New Faculty Award Program, and the Florida State University through time granted on its Cray Y-MP digital computer. The authors thank Dr. S. T. Mixon for the critical comments on the manuscript.

Cyclopentenone Formation via Hydrogen Activation in the Reactions of Chromium Carbene Complexes with Alkynes[1]

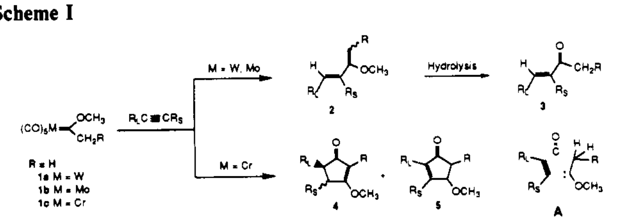
Cynthia A. Challener,[†,2a] William D. Wulff,[*,†] Benjamin A. Anderson,[†] Steve Chamberlin,[†,2b] Katherine L. Faron,[†,2a] Oak K. Kim,[†] Christopher K. Murray,[†] Yao-Chang Xu,[†] Dominic C. Yang,[†,2a] and Stephen D. Darling[‡]

Contribution from the Department of Chemistry, Searle Chemistry Laboratory, The University of Chicago, Chicago, Illinois 60637, and Department of Chemistry, University of Akron, Akron, Ohio 44325. *Received July 2, 1992*

Abstract: The reactions of alkyl chromium carbene complexes with alkynes have been found to give cyclopentenones. Mechanisms are proposed to account for the formation of these products that involve metal hydride intermediates. As has been previously reported for tungsten, molybdenum alkyl complexes have been found to give 1,3-dienes rather than cyclopentenones. The difference between chromium and molybdenum and tungsten may be that a metal hydride intermediate can re-add to an olefin in the case of chromium rather than undergo reductive elimination. A mechanism for the formation of cyclopentenones involving a free vinylketene was ruled out on the basis of an experiment in which the free vinylketene was generated via thermolysis of a cyclobutenone and found not to give a cyclopentenone product but rather an intramolecular [2 + 2] cycloadduct.

The coupling reactions of alkyl-substituted transition metal carbene complexes and alkynes have been known for some time.[3] The first reaction of this type involving activation of an α-hydrogen of the alkyl substituent was reported by Macomber in 1984.[4] He reported that (methylmethoxycarbene)pentacarbonyltungsten (**1a**, R = H) reacts with alkynes to provide moderate yields of 1,3-dienes (**2**) or the corresponding enones (**3**) after hydrolysis. Unlike the case for tungsten, there are no known reactions of alkyl-substituted molybdenum or chromium complexes with alkynes that involve activation of an α-hydrogen.[5] We report herein that all of the group 6 metals will react with acetylenes to give products resulting from activation of an α-hydrogen and that chromium

Scheme I

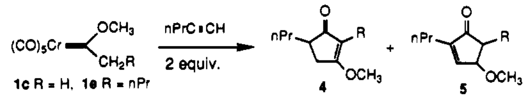


complexes uniquely produce the cyclic cyclopentenones **4** and **5** from this process.[1,6]

† The University of Chicago.
‡ University of Akron.

(1) A preliminary account of this work was presented at the American Chemical Society National Meeting in Dallas, Texas, on April 9–14, 1989, ORG 185.

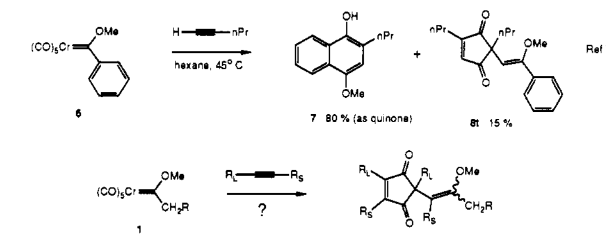
Table I. Effects of Solvent and Concentration on Cyclopentenone Formation[a]



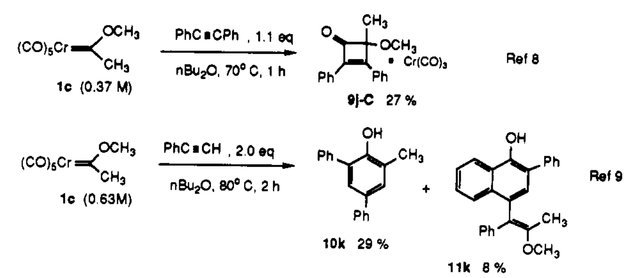
series	R	solvent	[1] (M)	% yield 4 + 5	4:5	other products
a	H	THF	0.06	≤9	only 4	
a	H	hexane	0.05	28	only 4	**8a** (5%)
a	H	hexane	0.50	≤2	only 4	**8a** (2%), **10a** + **16a** (≤4%)
n	nPr	THF	0.06	≤16	69:31	**13n** (≤7%), **14n** (5%)
n	nPr	hexane	0.05	25	92:8	**8n** (3%), **10n** + **16n** (≤5%)
n	nPr	hexane	0.20	15	only 4	
n	nPr	hexane	0.05	22[b]	only 4	**8n** (<5%)
n	nPr	hexane	0.05	<28[c,d]	>23:5	**8n** (<5%)
n	nPr	hexane	0.05	<2[e]		**17'n** (18%)

[a] Unless otherwise specified all reactions were carried out under argon at 70–80 °C with 2 equiv of alkyne. [b] With 2 equiv of PPh_3. [c] **4** (23%), **5** (<5%). [d] Under 1 atm of CO. [e] Under 100 atm of CO.

Scheme II



Scheme III



The present study was prompted by the observation that the phenylcarbene complex **6** will react with 1-pentyne in hexane solvent to give, in addition to the normal annulation product **7**, the cyclopentenedione **8t**, which has incorporated 2 equiv of the alkyne.[7] The formation of the cyclopentenedione products was found to be favored in intramolecular reactions where they can be the major products. Cyclopentendione formation is also favored in nonpolar, noncoordinating solvents: the reaction of **6** with 1-pentyne in THF does not produce any detectable amount of cyclopentenedione **8t**. As is the case of the reaction of **6** with 1-pentyne, the major product from the reactions of arylcarbene complexes with alkynes in the general case results from annulation onto the aryl ring to produce naphthols of the type **7**. However, if the aryl group in **6** were to be replaced by a simple alkyl group (i.e. complex **1**), then annulation would be obviated and thus it might be anticipated that cyclopentenediones would be obtained as major products from these reactions.

Prior to this work there were two reports of the reactions of alkylcarbene complexes with simple alkynes in which cyclic products were produced (with the exception of cyclopropyl complexes which lead to unique reaction pathways[6]). It has been observed that the methylcarbene complex **1c** will react with diphenylacetylene[8] to give the cyclobutenone chromium tricarbonyl complex **9j-C** and with phenylacetylene[9] to give the phenol **10k** and the naphthol **11k**, both of which have incorporated 2 equiv of the alkyne. These reactions of alkylcarbene complexes with alkynes were run in an ethereal solvent at high concentrations and, on the basis of what is known about the reaction of carbene complex **6** with 1-pentyne (Scheme II), were not run under conditions that would be ideal for cyclopentenedione formation. With these observations as precedent, this study was initiated for the purpose of more carefully examining the scope of the reactions of alkylcarbene complexes of the Fischer type with alkynes.

Reactions of Alkylcarbene Complexes with Alkynes

The reactions of alkylcarbene complexes with alkynes were found to be chemoselective, but not for the production of cyclopentenediones, cyclobutenones, or two-alkyne phenols, as would have been anticipated from the early studies. Instead, the major products from every reaction listed in Table II (except entry k) are the cyclopentenones **4** and **5**, which are derived from the pieces indicated in structure A where an α C–H bond is broken. These types of products had not been previously observed from the reactions of simple alkyl complexes with alkynes, although it is rather interesting that these same types of compounds have been observed from the reactions of cyclopropylcarbene complexes with alkynes in a reaction that is not mechanistically related (vide infra).[6]

(2) (a) National Institute of Health Predoctoral Fellow. (b) American Chemical Society Organic Division American Cyanamid Fellow 1991–1992.

(3) For recent reviews on the chemistry of carbene complexes, see: (a) Dotz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Dotz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisciplinary Field*; tom Dieck, H., de Meijere, A., Eds.; Springer: Berlin, 1988. (d) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (e) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press, Inc.: Greenwich, CT, 1989; Vol. 1. (f) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989. (g) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5.

(4) (a) Macomber, D. W. *Organometallics* **1984**, *3*, 1589. (b) A second example has appeared. Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc., Dalton Trans.* **1987**, 1041.

(5) (a) For activation of a hydrogen on a carbon α to the heteroatom substituent, see: Audouin, M.; Blandinieres, S.; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1990**, 23. (b) Since our initial report,[1] a cyclopentenone has been observed as a side-product from the reaction of the methyl chromium carbene complex **1c** with a 1,3-nonadien-8-yne: (c) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066.

(6) Recently it has been discovered that cyclopentenones of the type **4** and **5** are formed from the reaction of cyclopropyl chromium carbene complexes with alkynes in a process that is mechanistically unrelated: (a) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334. (b) Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, *30*, 295. (c) Herndon, J. W.; Matsui, J. J. *J. Org. Chem.* **1990**, *55*, 786.

(7) Xu, Y. C.; Challener, C. A.; Dragasich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269.

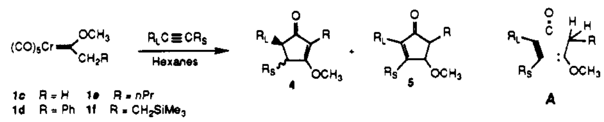
(8) Dotz, K. H.; Dietz, R. E. *J. Organomet. Chem.* **1978**, *157*, C55.

(9) (a) Dietz, R.; Dotz, K. H.; Neugebauer, D. *Nouv. J. Chim.* **1978**, *2*, 59. (b) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

(10) (a) Dötz, K. H.; *J. Organomet. Chem.* **1977**, *140*, 177. (b) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520. (c) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. (d) Semmelhack, M. F.; Jeong, N.; Lee, G. R. *Tetrahedron Lett.* **1990**, *31*, 609.

(11) Bos, M. E.; Wulff, W. D.; Brandvold, T. A.; Chamberlin, S.; Miller, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293.

Table II. Cyclopentenones from Alkyl Chromium Carbene Complexes[a]



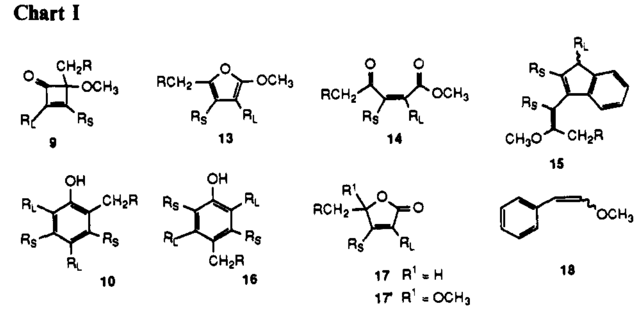
entry	R	R_S	R_L	% yield	product ratio *trans*-**4**	*cis*-**4**	**5**
a	H	H	nPr	28[b]	100		
b		H	iPr	23[c]	100		
c		H	tBu	23[d]	100		
d		Et	Et	42	72	10	18
e		nPr	nPr	57[e]	67[f]		33
f		nPen	nPen	58	59		41
g		nHex	nHex	50	58[g]		42
h		nHep	nHep	51	63[h]		37
i		H	R^i	52	100		
j		Ph	Ph	36[j,k]	43	21	36
k		H	Ph	7[l]	100		
l		Ph	Me	25[m]	64		36
m		Me	R^n	36[n]	42		58
n	nPr	H	nPr	25[o]	92		8
o		H	iPr	20[p]	95		5
p		H	tBu	36[q]	92		8
q		Ph	Ph	38[r]	68	8	24
r	Ph	H	tBu	28[s]	100		
s	CH_2SiMe_3	H	tBu	34[t]	100		
t		Ph	Ph	60[u]	80		20

[a] Unless otherwise specified all reactions were run in hexane at 0.05 M in carbene complex with 1–2 equiv of alkyne at 60–100 °C for 12–24 h. [b] Also a 5% yield of **8a**. [c] Also a 4% yield of **8b**. [d] Also a 6% yield of **8c**. [e] A 56% total yield of essentially the same ratio of products was obtained in 1% aqueous dioxane with 2 equiv of alkyne added via syringe pump (ref 6). [f] A 5:2 mixture of isomers **4e**. [g] A 2:1 mixture of isomers **4f**. [h] A 5.6:1 mixture of isomers **4g**. [i] R = $CH(CH_3)CH_2CH_2C(CH_3){=}CH_2$ (alkyne **25**); also a 14% yield of **14i**. [j] nBu_2O solvent; also a 4% yield of **13j** and a 10% yield of **9j**. [k] See text for other examples of this reaction. [l] Also a 34% yield of a 1.8:1 mixture of phenols **10k** and **11k**. [m] In THF solvent at 0.08 M in **1c**; 11% *trans*-**4l**, 3% *cis*-**4l**, 26% **5l**, 8% **9l**. [n] R = $CH_2CH_2OCH_2OCH_3$; both **4m** and **5m** isolated as 1.4:1 mixtures of isomers, regiochemistry not determined. [o] Also a 3% yield of **8n** and ~5% yield of phenols **10n** and **16n**. [p] Also a 2% yield of **8o**. [q] Also a 6% yield of **8p**. [r] Workup with $FeCl_3$–DMF complex; also an 8% yield of **14q**. [s] 0.02 M in **1d**; also a 7% yield of **8r** and a small amount of **18**. [t] 45 °C; in a separate reaction, the yield of **8s** was determined to be 6%. [u] Includes an 8% yield of 55.

The optimal conditions for the formation of the cyclopentenone products were found to be with hexane as solvent, with a concentration of carbene complex of 0.05 M, and with 2 equiv of alkyne. These are the conditions under which all of the reactions in Table II were carried out and which typically took 8–20 h at 70–80 °C. Only poor yields of cyclopentenones are produced from reactions with simple terminal alkynes, and it was for this reason that the optimal conditions were determined for the reactions of the alkyl complexes **1c** and **1e** with 1-pentyne, as shown by the data in Table I. The reaction of **1c** with 1-pentyne gave the cyclopentenone **4a** in less than 9% yield in THF, but this could be improved to 28% if the reaction solvent was changed to hexane. For terminal acetylenes the vinylogous ester **4** is the major or exclusive product and the other conjugated isomer **5** is rarely observed if at all. The structure of **4a** was confirmed by comparison of its spectral data with those of an authentic sample prepared by the alkylation of 3-methoxycyclopentenone with *n*-propyl bromide. The yield of cyclopentenone **4** is dependent on the concentration although this is true more so for the methyl complex **1c** than for the butyl complex **1e**. The yield of **4a** drops to nearly zero upon raising the concentration from 0.05 to 0.5 M, but for the butyl complex the yield of **4n** decreases from 25% to 15% when the concentration is raised from 0.05 to 0.2 M. There is no apparent concentration dependence for the reaction of the butyl complex **1e** with either isopropylacetylene or *tert*-butylacetylene (Table II, entries o and p) over an even greater concentration range. As indicated by the data in Table I, the distribution of products is not affected by the presence of either 2 equiv of triphenylphosphine or 1 atm of carbon monoxide. However, under 100 atm of carbon monoxide, the product distribution from the reaction of **1e** with 1-pentyne is diverted from the cyclopentenones **4** and **5** to the lactone **17n**.[12]

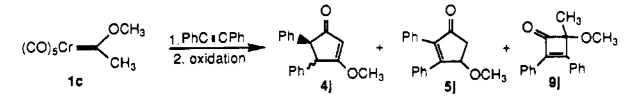
(12) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

Chart I



In addition to the cyclopentenones **4** and **5**, a number of minor products have been observed from the reactions in Tables I and II. The products indicated in the tables are those that are observable by TLC, ¹H NMR, and in some cases GC, and thus the remainder of the mass balance must be due to material that is insoluble and/or not mobile on silica gel. The cyclopentenediones **8**, which were anticipated to be the major products from the reactions of alkylcarbene complexes with alkynes in hexane solvent, are in fact formed in a number of reactions in Tables I and II but always as a minor product and never in more than 7% yield. The cyclopentenedione **8t** was determined to be the *Z*-olefin isomer by NOE experiments; however, the stereochemistry of the olefins in the cyclopentenediones obtained as minor products in the present work was not determined. Other minor products observed from the reactions listed in Tables I and II include the furan[10,11] **13** and its oxidation product **14**, the two-alkyne phenols[7,9b] **10**, **11**, and **16**, the indene **15**, and the cyclobutenone[8,12] **9** (Chart I). The reactions listed in Tables I and II were carried out and analyzed most carefully for the cyclopentenones **4** and **5** and the cyclopentenedione **8**, which typically are the most polar of all of the products observed in these reactions. No attempt was made to determine the yields of the nonpolar products (such as the furan **13** and the two-alkyne phenols **10** and **16**) from each reaction in

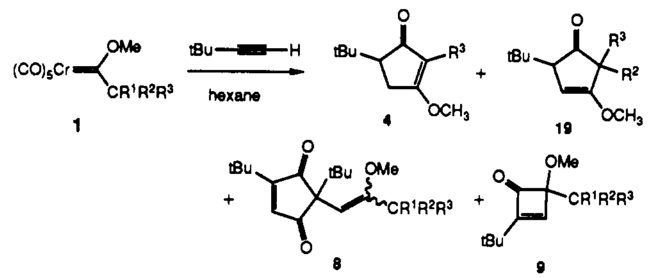
Table III. Products from the Reaction of Complex **1c** with Diphenylacetylene[a]



entry	solvent	[1c] (M)	oxidant	% yield **4j**, t:c	**5j**	**9j**	**13j**	**14j**	**15j**
1	nBu_2O	0.37	air	10, trans	5	17	4		
2	nBu_2O	0.37	Fe^{3+}	6, trans	3	25		6	
3	nBu_2O	0.37	Ce^{4+}	9, trans	4	15			
4	nBu_2O	0.05	air	23, 2:1	13	10			
5	hexane	0.05	Fe^{3+}	13, 2,3:1	9	11		imp	7

[a] Reaction conditions as in Table II.

Table IV. Product Distributions from Complexes with Primary, Secondary, and α-Hydrogens[a]



complex	R^1	R^2	R^3	ratio of products **4**	**19**	**8**[b]	**9**	total % yield	product series
1c	H	H	H	79		21		29	c
1e	H	H	nPr	88[c]		12		41	p
1d	H	H	Ph	80		20		35	r
1f	H	H	CH_2SiMe_3	85		15		40	s
1g	H	Me	Me		33	36	31	33	u
1h	Me	Me	Me			49	51	52[d]	v

[a] Reaction conditions as in Table II. [b] Stereochemistry not determined. [c] 33% **4p** and 3% **5p**. [d] Includes 1% **10v** and 8% **17v**.

Tables I and II. β-Methoxystyrene **18** was detected in the crude mixture from the reaction of the benzyl complex **1d** with *tert*-butylacetylene. This product presumably resulted from the decomposition of the benzyl complex **1d**, and its presence was confirmed by carrying out an α-elimination reaction according to the procedure first reported by E. O. Fischer involving the treatment of the carbene complex **1d** with pyridine.[13] Surprisingly, although the simple alkyl complexes examined by Fischer provided *trans*-enol ethers as the major product, the base-induced β-elimination of the benzyl complex **1d** produced a 3.3:1 mixture of the *cis*- and *trans*-β-methoxystyrenes **18** in 44% yield.

For the historical reasons outlined in the introduction, the reaction of the methyl complex with diphenylacetylene was investigated under a variety of conditions and the results are summarized in Table III. Under the conditions (*n*-butyl ether, 0.37 M) for which this reaction was originally investigated and reported[8] to give the cyclobutenone chromium tricarbonyl complex **9j-C** (Scheme III), we also find the cyclopentenones **4j** and **5j** and the furan **13j**. When oxidation of the crude reaction mixture was carried out with Fe^{3+} to remove the metal from the desired organic products, the yields of cyclopentenones dropped significantly while cyclobutenone formation increased to 25%. The observations can most easily be explained by suggesting that air oxidation is ineffective in removing the metal from the cyclobutenone **9j** and that the cyclopentenones **4j** and **5j** are not completely stable to Fe^{3+} (or Ce^{4+}). The best yield of cyclopentenone was obtained at lower concentration in carbene complex with air oxidation only. The reaction in hexane at low concentration and Fe^{3+} oxidation gave similar yields as the reaction in ether solvent. The indene **15j** formed only when the reaction was run in hexane.[14] Although the cyclopentenones are the major products when the starting concentration of carbene complex is 0.05 M, the cyclobutenones are still significant side products from the reaction of **1c** with diphenylacetylene and this is not the case with any of the other reactions in Table I. The propensity for diphenylacetylene and other sterically bulky acetylenes to give cyclobutenone products has been previously noted and discussed.[12]

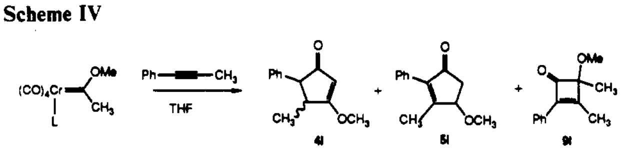
The reaction of complex **1c** with phenylacetylene was also reinvestigated. When this reaction was carried out in hexane according to the standard conditions described in Table II, the phenol **10k** and the naphthol **11k** were formed in nearly the same yields (22% and 12%, respectively) as those for the reaction in *n*-butyl ether that is described in the original reports on the reaction (Scheme III).[9] Only a small amount of the cyclopentenone **4k** (7%) was formed in this reaction, so this reaction is thus the only example in Table I in which cyclopentenones are not the major product from the reaction of an alkylcarbene complex in hexane solvent.

The set of experiments outlined in Table IV were designed to examine the relative abilities of primary, secondary, and tertiary hydrogens to be activated in the process that leads to cyclopentenone products. In the first four entries in the table, the only products that could be isolated were the cyclopentenone **4** and the cyclopentenedione **8**. The ratio of the C–H activated product **4** to the non-C–H activated product **8** is essentially the same for the situations where the α-hydrogen is primary, secondary, benzylic, and also β-silyl. When the α-hydrogen is tertiary, as in the isopropyl complex **1g**, reduced proportions of the C–H activated product relative to the non-C–H activation products **8u** and **9u** are obtained. The *tert*-butyl complex **1h** serves as a control experiment, since C–H activation is not possible. The trends seen in these reactions do not correlate with the insertions of free carbenes into C–H bonds nor with the relative bond strengths of primary, secondary, and tertiary hydrogens. The lack of a sig-

(13) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1973**, *107*, 3326.

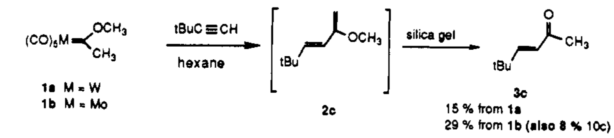
(14) This product is a non-CO-inserted version of the structural type that has been observed previously in the compound **11k**.[9]

Scheme IV



Complex	L	Temp (°C)	time (h)	Atmosphere	4l	5l	9l	Total Yield
1c	CO	70	24	argon	29	54	17	48
20	PPh_3	22	12	argon			100	20
1c	CO	70	17	CO (1 atm)	53	35	12	54

Scheme V



nificant effect of an α-phenyl group or a β-silyl group suggests that the C–H bond is not broken in a polarized manner which has been observed for β-hydride eliminations in organometallic systems.[15] The reduced proportion of C–H activated product from the complex **1g** is likely related to the steric effects of the conformational preferences of the isopropyl group.

The presence of triphenylphosphine did not affect the outcome of the reaction of the methyl complex **1c** with 1-pentyne (Table I, entry 7). However, replacement of one of the CO ligands in the pentacarbonyl complex **1c** with triphenylphosphine does dramatically affect the outcome of the reaction with phenylpropyne as indicated in Scheme IV. In this reaction the formation of the cyclopentenone products is completely suppressed and the only isolable product is the cyclobutenone **9l**. The product distribution from the reaction of the pentacarbonyl complex **1c** with phenylpropyne is not affected by 1 atm of carbon monoxide. This same observation was made for the reaction of complex **1c** with 1-pentyne (Table I, entry 8), although in this case, under 100 psi of carbon monoxide, the formation of cyclopentenone products was suppressed (Table I, entry 9). The difference in the effect of the coordinated phosphine in the reaction of **20** and that of external phosphine in the reaction in entry 7 in Table I is quite interesting and may be related to issues that have previously been defined in the formation of cyclobutenones.[12]

The reaction of the methyl chromium complex **1c** with *tert*-butylacetylene gives the cyclopentenone **4c** and the cyclopentenedione **8c** (Table II, entry c). The same reactions of the corresponding tungsten and molybdenum complexes **1a** and **1b** give the acyclic enone **3c** as the only isolable product. It has been previously shown that alkyl tungsten carbene complexes will give enone products of the type **3** and that they are secondary products resulting from the hydrolysis of the dienes of the type **2**, which are the primary products of the reaction.[4] C–H activation reactions of alkyl molybdenum carbene complexes with alkynes have not been previously reported.[16] Here it is found that none of the cyclopentenone product **4c** or the cyclopentenedione product **8c** could be detected from the reaction of either the tungsten or molybdenum complexes **1a** or **1b** with *tert*-butylacetylene. Furthermore, the presence of diene or acyclic enone products of the type **2** or **3** has not been detected from any reaction of an alkyl chromium carbene complex and an alkyne.

To obtain even moderate yields of cyclopentenones, the heteroatom substituent on the chromium alkyl complex must be an oxygen-containing group. As indicated in Scheme VI, thioether complexes also provide cyclopentenones, but the yields are extremely low. Simple amino complexes such as **24** (Scheme VI) provide the same enone derived from reductive elimination as do the molybdenum and tungsten complexes. The reaction of **24** with *tert*-butylacetylene gives the acyclic enone **3c** in 15% yield as the only isolable product with no evidence for the formation of cyclopentenone products. The reaction of alkyl imidate complexes with alkynes was originally investigated as a route to 3-hydroxypyridines.[17] The reaction of the complex **22** with 1-pentyne did produce the 3-hydroxypyridine **23** in 21% yield but also gave the cyclopentenone **4x** in 18% yield.

From the synthetic point of view, the reaction is most useful with disubstituted alkynes or with terminal alkynes with long side chains, as indicated by the reactions in Scheme VII. The reaction of **1c** with the alkyne **25** produces the cyclopentenone **4i** in 52% yield. The increased yield of **4i** over cyclopentenones from other terminal acetylenes is not due to steric hindrance at the propargylic position, since 1-pentyne, isopropylacetylene, and *tert*-butylacetylene all give similar results with complex **1c**, as indicated in Table II. The greater efficiency with alkyne **25** may be due to the long side chain or to the presence of the alkene function in the side chain. This issue will be addressed in future work, and preliminary results suggest it is due to the presence of the alkene function. The reaction of complex **1c** with 4-octyne gives a mixture of the cyclopentenones **4e** and **5e** in 57% yield. It can be seen from the data in Table II that the reactions with internal alkynes are uniformly of greater efficiency than the reactions with terminal alkynes. Although these reactions with internal alkynes generally produce mixtures of the regioisomeric enones **4** and **5**, the vinylogous ester **4** is the thermodynamic product and it has previously been shown that a mixture of **4j** and **5j** can be converted to exclusively **4j** with sodium methoxide,[6a] thus increasing the potential applications of these reactions.

The mechanistic possibilities for cyclopentenone formation shown in Scheme VIII are all related in the first steps to a mechanism that has been proposed for the formation of dienes of the type **2** from the reactions of alkyl tungsten carbene complexes with alkynes.[4] The formation of the diene **2** was proposed to occur via a β-hydride elimination from the metallacyclobutene intermediate **26** followed by a reductive elimination from the dienyl metal hydride **28**.[4a] An alternate explanation involving an initial electrocyclic ring opening of **26** to the vinylcarbene complex intermediate **27** and a subsequent 1,5-sigmatropic shift of hydrogen could not be ruled out. It should be pointed out that recent calculations by Hofmann[18] suggest that, upon loss of CO from complex **1**, there is a direct reaction with the alkyne to produce intermediate **27** without the intervention of the metallacyclobutenone **26**. If the vinylcarbene complexed intermediate **27** really has the metal bonded to all three carbons, the issue of whether the metal hydride intermediate **28** is formed by a β-elimination or by a 1,5-sigmatropic shift of hydrogen becomes a distinction with a much finer line.

As indicated in Scheme V, the reactions of alkyl molybdenum carbene complexes with alkynes lead to the formation of dienes of the type **2**, as has been reported for alkyl tungsten complexes.[4] The corresponding reactions of alkyl chromium complexes are quite distinct from those of molybdenum and tungsten. We have not detected dienes of the type **2**, or products derived therefrom, from any reaction of an alkyl chromium complex. Apparently if the same intermediate **28** is involved, the reactions of the chromium complexes differ from those of tungsten and molybdenum in that the chromium hydride unit re-adds to the olefin in **28** in the direction opposite to that of the β-hydride elimination from whence it was formed. This re-addition can occur at the intermediate **28** to give the metallacyclopentene **29** followed by CO insertion and reductive elimination to give the cyclopentenone complex **34**. Alternatively, re-addition of the metal hydride can occur at the intermediate **31** (formed by CO insertion in **28**), generating the η^3-allylcyclopentanone complex **34**. An alternate mechanism that must be considered involves the oxidative addition to the allylic hydrogen[19] in the vinylketene complex **30**, which

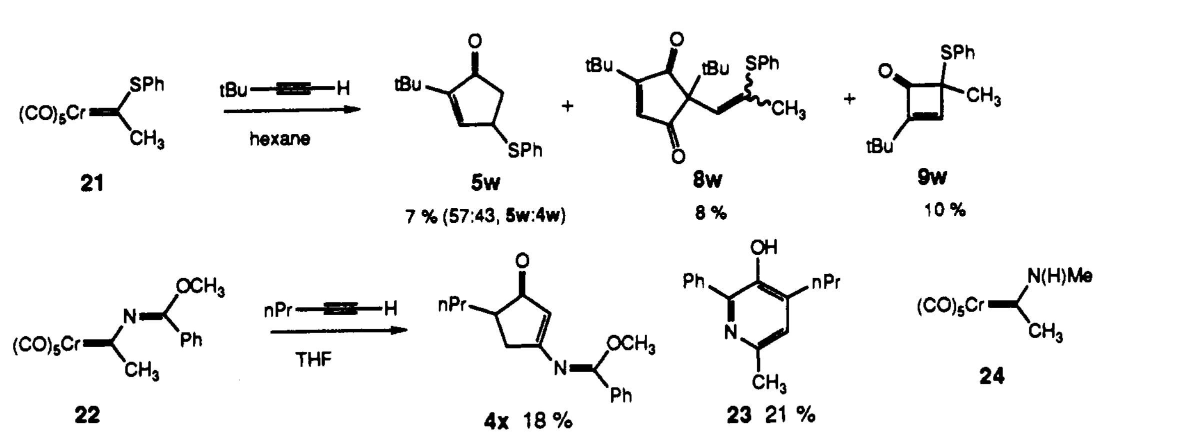
(15) (a) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (b) Buchwald, S. L.; Nielson, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171.

(16) Intramolecular reactions of alkyl molybdenum complexes with alkynes have been reported. Brandvold, T. A.; Wulff, W. D.; Rhiengold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1645. Intermolecular reactions of alkyl molybdenum complexes with alkynes have been reported for diynes[9b] and dienynes.[5c]

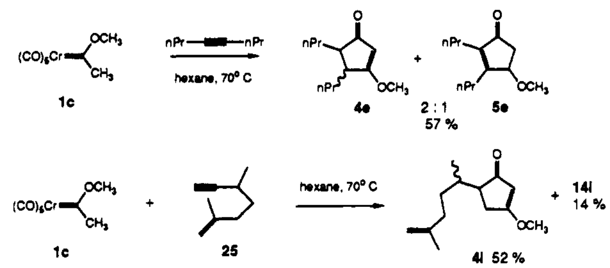
(17) (a) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251. (b) Wulff, W. D.; Dragisich, V.; Huffman, J. C.; Kaesler, R. W.; Yang, D. C. *Organometallics* **1989**, *8*, 2196.

(18) Hofmann, P.; Hammerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908.

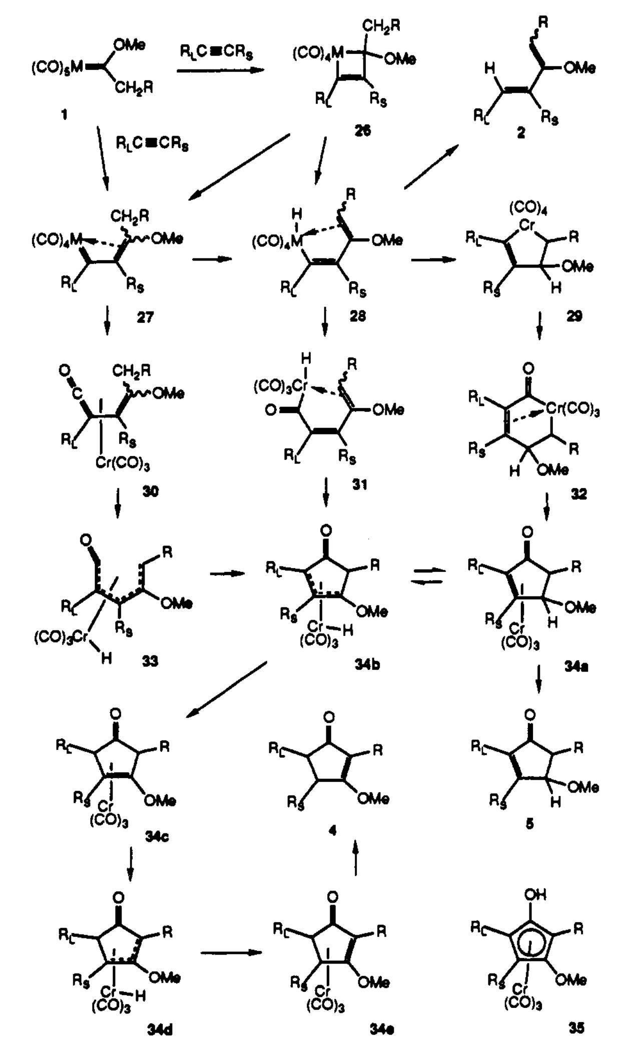
Scheme VI



Scheme VII

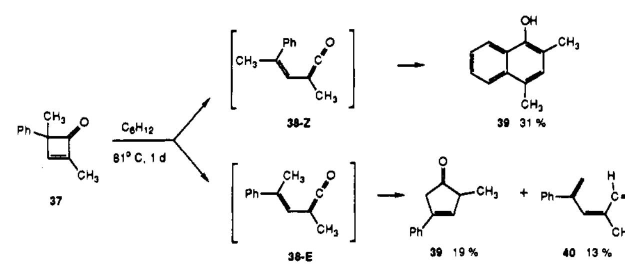


Scheme VIII

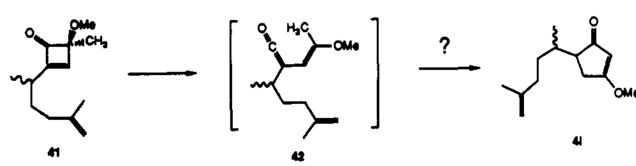


generates the η^5-pentadienoyl complex **33**, which undergoes ring closure to **34**. Such a ring closure of an η^5-pentadienoyl complex has been reported for an organocobalt complex,[20a] and an iron η^5-pentadienoyl complex has recently been detected as an intermediate in a process that presumably involves a ring closure to give an η^3-allylcyclopentanone complex of the type **34b**.[20b]

Scheme IX



Scheme X



Another mechanism that must also be considered involves the intermediacy of a free vinylketene. The cyclobutenone **37** has been shown to thermally ring open to give two isomeric vinylketene intermediates (Scheme IX).[21] The vinylketene **38-Z** cyclizes to naphthol **39** in 31% yield. The vinylketene **38-E** gives the cyclopentenone **39** and the dienyl aldehyde **40**. A mechanism to account for the formation of the cyclopentenone **39** was not presented, but it was shown not be be derived from the aldehyde **40**. Metal complexed vinylketene intermediates have been proposed[22] to be involved in the reactions of group 6 Fischer carbene complexes and alkynes in a number of situations; however, it is possible that the cyclopentenones **4** and **5** are not formed from any of the mechanisms involving metal hydride intermediates in Scheme VIII but rather from a free vinylketene which could be generated via ligand displacement from the intermediate **30**.

An opportunity to test for the intermediacy of a free vinylketene was made possible by the reaction of complex **1a** and the 1,6-heptenyne **25** (Scheme VII). The formation of cyclopentenone **4i** from this reaction was surprising, since reactions with 1,6-heptenynes normally give cyclopropanes or cyclobutanones.[23] The

(19) Michael, G.; Kaub, J.; Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 502.

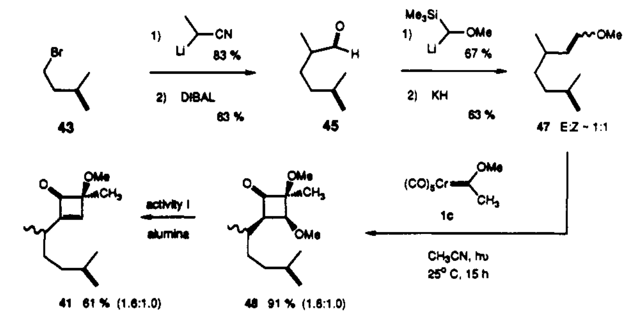
(20) (a) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3387. (b) Yongskulrote, W.; Bramlett, J. M.; Mike, C. A.; Durham, B.; Allison, N. T. *Organometallics* **1989**, *8*, 556. See also: Dawson, D. P.; Allison, N. T. *J. Am. Chem. Soc.*, in press.

(21) Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 500.

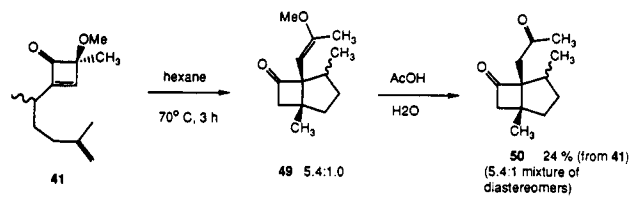
(22) For leading references, see: Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615.

(23) (a) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461. (b) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676.

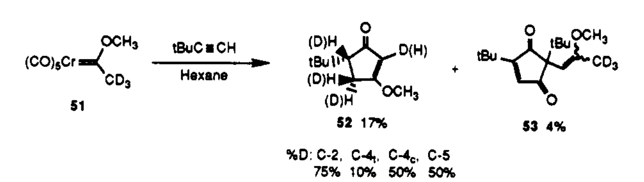
Scheme XI



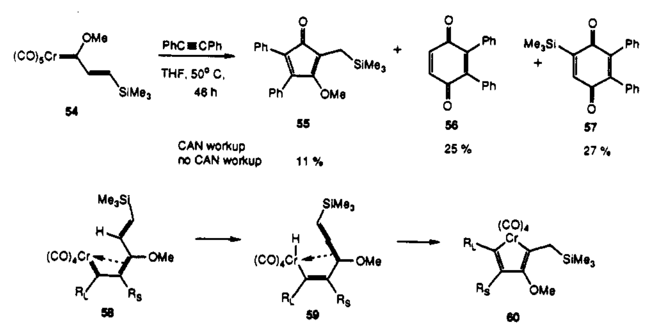
Scheme XII



Scheme XIII



Scheme XIV



free vinylketene that would give rise to the cyclopentenone **4i** is the ketene **42**, and evidence for or against its involvement in the formation of cyclopentenone **4i** from the reaction of carbene complex **1c** and alkyne **25** could be obtained from an experiment in which ketene **42** was generated in a nonorganometallic reaction. A thermally induced electrocyclic ring opening of cyclobutenones is one of the most convenient methods for the generation of vinylketenes. For the case of the vinylketene **42**, the *E*-geometry of the vinylketene **42** would be anticipated from the ring opening of the cyclobutenone **41**, since it is well established that alkoxycyclobutenones[24] and alkoxycyclobutenes[25] undergo electrocyclic ring opening with outward rotation of the alkoxyl group.

After more traditional routes failed, a successful synthesis of cyclobutenone **41** was achieved in which the key step involved a [2 + 2] cycloaddition of a ketene generated from the photolysis of the carbene complex **1c**. This reaction has recently been reported by Sierra and Hegedus as an efficient method for the preparation of cyclobutenones.[26] The requisite enol ether **47** was prepared from 4-bromo-2-methyl-1-butene in the four steps that are indicated in Scheme XI. The enol ether **47** was obtained as ~1:1 mixture of isomers from the aldehyde **45** in a Peterson synthesis;[27] however, it was found that only the *Z*-isomer of **47** would undergo [2 + 2] cycloaddition with the ketene that was generated from the carbene complex **1c**, and thus the separation of isomers was unnecessary. The cyclobutanone **48** was obtained as a 1.6:1.0 mixture of only two of the possible eight diastereomers which are epimeric at the exocyclic methine carbon. This is consistent with the observations of Sierra and Hegedus where they found that the formation of cyclobutanones from enol ethers is highly stereoselective and stereospecific in favor of the syn isomer, which is the basis for the assignment of the stereochemistry of **48**. The desired cyclobutenone **41** can be obtained in good yield by elimination of methanol from **48** that is induced by rapid elution through activity I alumina. The cyclobutenone **41** is also obtained as a 1.6:1.0 mixture of diastereomers, thus confirming the position of the epimeric carbon in the cyclobutanone **48**.

That the formation of **4i** does not involve the free vinylketene **42-E** was demonstrated by the thermolysis of the cyclobutenone **41**, which gave the intramolecular [2 + 2] cycloadduct **49** as a 5.4:1 mixture of stereoisomers. The two diastereomers of **49** involve epimers at the C-2 methyl rather than geometrical isomers about the double bond. This was confirmed by the hydrolysis of the mixture of isomers of **49** to give a 5.4:1 mixture of two diketones **50** (24% overall from **41**) and by NOE experiments on and ^{13}C NMR spectra[28] of each of the isomers of **49**, which revealed that both are *E*-enol ethers. Thus as expected, the electrocyclic ring opening of **41** occurs exclusively with an outward rotation of the methoxyl group to generate only the *E*-isomer of the vinylketene **42**. While the yield of **49** is low, no other products could be detected from this reaction, and from the ^1H NMR spectrum of the crude reaction mixture, the cyclopentenone **4i** could not have been formed in more than 0.3% yield. The 24% yield of **50** is in fact approximately what would be expected on the basis of the efficiency of the intramolecular [2 + 2] cycloadditions of ketenes and alkenes.[29] The metal-free *E*-vinylketene **42** thus clearly prefers to undergo an intramolecular [2 + 2] cycloaddition with the pendant alkene rather than rearrange to the cyclopentenone **4i**. Thus if the formation of the cyclopentenone **4i** does involve the intermediacy of a vinylketene, it must be maintained in the coordination sphere of the metal; i.e., the activation of the α-hydrogen is mediated by the metal. It is possible that the metal is coordinated to the olefin in the free ketene in **42** (Scheme X) and prevents the [2 + 2] cycloaddition, but this is not considered to be very likely, since simple alkenes are very poor ligands for group 6 metal carbonyl complexes.[47,48]

While the mechanism for the formation of cyclopentenones involving a free vinylketene can be ruled out on the basis of the above experiment, at this time, there is no data to distinguish between the two mechanisms indicated in Scheme VIII, where the α-hydrogen is either activated in the vinylketene complex **30** or the vinylcarbene complex **27**. Nonetheless, the reaction of the deuterated complex **51** with *tert*-butylacetylene indicated in Scheme XIII sheds some light on the last steps of the reaction. This reaction produces the deuterated cyclopentenone **52**, in which the deuterium is found to be scrambled at all four positions, as indicated in the scheme. This result would be consistent with the intermediacy of **34a–e** and the fact that these intermediates are readily interconverted. Although we have no evidence in support, it is interesting to consider the possibility that these intermediates are interconverted via the hydroxycyclopentadienyl complex **35**.[20b]

In an unrelated study, we serendipitously found an example of the activation of an α-hydrogen on an sp^2-hybridized carbon in the reaction of the (β-(trimethylsily)vinyl)carbene complex **54** with diphenylacetylene. In addition to the expected benzannulated products **56** and **57**, this reaction also produced the cyclopentadienone **55**, whose structure was confirmed by an X-ray diffraction analysis. It is interesting that despite the fact that a large number of benzannulations of vinylcarbene complexes and

(24) For leading citations, see: (a) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482. (b) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

(25) Houk, K. N.; Spellmeyer, D. C.; Jefford, C. W.; Rimbault, C. G.; Wang, Y.; Miller, R. D. *J. Org. Chem.* **1988**, *53*, 2127.

(26) Sierra, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1989**, *111*, 2335.

(27) Magnus, P.; Roy, G. *Organometallics* **1982**, *1*, 553.

(28) Strobel, M. P.; Andrieu, c. G.; Paquer, D.; Vazeux, M.; Pham, C. C. *Nouv. J. Chim.* **1980**, *4*, 101.

(29) Snider, B. B.; *Chem. Rev.* **1988**, *88*, 793.

alkynes have been investigated, cyclopentadienones have never been reported previously from this reaction. Since this is the first time that the benzannulation of a (β-silylvinyl)carbene complex has been examined, it is tempting to conclude that the formation of the cyclopentadienone product is facilitated by the presence of the silyl group on the β-position of the vinylcarbene complex. If this is in fact the case, the reason for the activation by the silyl group may be related to the ease of the activation of the α-vinyl hydrogen in the vinylcarbene complex intermediate **58**, where the silicon substituent may facilitate hydrogen transfer to the metal center as a hydride, i.e., a mechanism involving some buildup of positive charge on the α-vinyl carbon β to the silicon.[30] The mechanisms of β-hydride eliminations have been observed to occur either via proton or hydride transfer.[15] However, if this effect of silicon is indeed real, the β-silylethyl complex **1f** should react with acetylenes to give greatly increased yields of cyclopentenones. Unfortunately, the yields are comparable to those obtained for the butyl methoxy complex **1e**; 60% for the silylethyl complex **1f** and 38% for the *n*-butyl complex **1e** when reacted with diphenylacetylene (Table II). Although one might argue that a noticeable increase in yield is obtained, the results with 3,3-dimethyl-1-butyne (Table II, entries p, 27%, and s, 34%) do not support this conclusion. The benzyl complex **1d** would also be expected to increase the yield of cyclopentenones whether the character of the transferred hydrogen was partially positive or negative. However, this reaction also shows no significant improvement in cyclopentenone formation (entry r, Table I). The results of these experiments do not provide evidence to support or discredit the existence of a β-hydride elimination step in these reactions.

The studies discussed in this paper reveal that all of the group 6 metal carbene complexes bearing an alkyl substituent will react with alkynes to give organic products in which the α-hydrogen of the alkyl group has been activated by a metal-mediated process. Chromium is unique in generating cyclic products from these reactions. Several possible mechanisms for this new transformation have been proposed, and experiments designed to test for the feasibility of the various pathways have been presented. Of the suggested mechanisms, the one involving formation of the cyclopentenones via a free vinylketene has been discounted, leaving only mechanisms that involve activation of the α-hydrogen by the metal center. The activation of an α-vinyl hydrogen in a chromium complex is also possible where the α-vinyl hydrogen is β to a silicon group. The reactivity of alkyl-substituted carbene complexes of the group 6 metals demonstrated herein serves to further underscore the complexity and variety of organometallic processes involved in the reactions of Fischer carbene complexes and alkynes.

Experimental Section

Unless otherwise indicated all common reagents and solvents were used as obtained from commercial suppliers without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. All melting points were determined in open capillary tubes using a Hoover melting point apparatus and are uncorrected. Routine ^{1}H NMR spectra (δ, ppm) were recorded on either a General Electric QE-300 MHz or a DS 1000 (Chicago built) 500 MHz spectrometer in $CDCl_3$. The ^{13}C NMR spectra (δ, ppm) were recorded on a Varian XL-400 spectrometer at 100 MHz or a General Electric QE-300 spectrometer at 75 MHz. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer. Low-resolution mass spectra were recorded on a Finnigan 1015 instrument, and high-resolution mass spectra were recorded on a VG 70-250 mass spectrometer or run by ICR Research Associates, Inc., Lincoln, NE, or the Midwest Center for Mass Spectrometry, Lincoln, NE. Elemental analyses were carried out by Galbraith Labs, Inc., Knoxville, TN, or Desert Analytics, Tucson, AZ.

General Procedure for the Reactions of Carbene Complexes with Alkynes. The carbene complex and 1–2 equiv of alkyne were placed in a single-necked flask equipped with a threaded high-vacuum stopcock and diluted with enough hexane to provide a 0.05 M solution in carbene complex. The mixture was then deoxygenated by the freeze–thaw method (−196 °C/25 °C, 3 cycles) and back filled with argon and the stopcock sealed at 25 °C. The reaction flask was heated at 70–100 °C (70–80 °C most typical) for 8–20 h. The solvent was then removed under vacuum on a rotary evaporator and the crude mixture purified by flash chromatography on silica gel. In some cases, especially with terminal alkynes, excesses of polymer were removed with bulb-to-bulb distillation prior to chromatography. Unless otherwise specified, the solvents for chromatography are a ternary mixture of ether, methylene chloride, and hexane.

Reaction of Pentacarbonyl(methoxymethylcarbene)chromium (1c) with 1-Pentyne. A solution of 0.120 g (0.48 mmol) of complex **1c**[31] and 0.065 g (0.96 mmol) of 1-pentyne in 9.6 mL of hexane was subjected to the general reaction conditions described above. This reaction provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.006 g (5%) of **8a** as a bright-yellow waxy semisolid and 0.020 g (28%) of **4a** as a volatile colorless oil. Spectral data for **4a**: ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, J = 7.3 Hz, Pr-CH_3), 1.30–1.40 (m, 3 H, CH(*H*)*CH*$_2$CH$_3$), 1.76–1.84 (m, 1 H, *C*H(H)CH$_2$CH$_3$), 2.28 (dd, 1 H, J = 17.7, 2.3 Hz, 4-CH_{trans}), 2.45–2.51 (m, 1 H, 5-CH), 2.73 (dd, 1 H, J = 17.7, 7.3 Hz, 4-CH_{cis}), 3.81 (s, 3 H, OCH_3), 5.24 (s, 1 H, 2-CH); ^{13}C NMR ($CDCl_3$) δ 13.95 (q, J = 124.7 Hz, CH_3), 20.32 (t, J = 126.5 Hz, CH_2), 33.54 (t, J = 126.5 Hz, CH_2), 34.69 (t, J = 129.7 Hz, CH_2), 45.32 (d, J = 130.0 Hz, C-5), 58.51 (q, J = 145.7 Hz, OCH_3), 103.62 (d, J = 169.5 Hz, C-2), 189.85 (s, C-3), 208.22 (s, C-1); IR (neat) 2964 s, 2947 s, 2873 s, 2852 s, 1698 s, 1602 s, 1458 s, 1378 s, 1354 s, 1285 m, 1241 s, 1189 m, 1164 s, 1000 s, 907 m, 820 m, 736 s cm^{-1}; mass spectrum, m/e (% relative intensity) 154 M$^+$ (4), 125 (11), 112 (100), 97 (15), 83 (37), 69 (14), 65 (3). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.76; H, 9.39. Spectral data for **8a** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 7.2 Hz, Pr-CH_3), 0.99 (t, 3 H, J = 7.4 Hz, Pr-CH_3), 1.10 (m, 2 H, *CH*$_2$CH$_3$), 1.60–1.70 (m, 4 H, 5-*CH*$_2$Et + *CH*$_2$CH$_3$), 1.77 (s, 3 H, CH_3), 2.43 (td, 2 H, J = 7.3, 1.0 Hz, 2-*CH*$_2$Et), 3.26 (s, 3 H, OCH_3), 4.35 (s, 1 H, 6-CH), 6.81 (d, 1 H, J = 0.9 Hz, 3-CH); ^{13}C NMR ($CDCl_3$) δ 13.82 (q, Pr-CH_3), 14.37 (q, Pr-CH_3), 16.45, 17.82, 20.45, 27.46, 37.46, 54.46, 54.57, 105.35 (d, C-3), 141.79 (d, C-6), 153.08 (s, C-2), 163.71 (s, C-7), 206.79 (s, C-1 or 4), 207.51 (C-1 or 4); IR (neat) 2961 m, 2934 m, 2875 m, 1743 m, 1699 s, 1616 m, 1457 m, 1437 m, 1381 m, 1331 m, 1214 m, 1163 m, 1091 m, 1059 m, 916 m, 732 m cm^{-1}; mass spectrum, m/e (% relative intensity) 250 M$^+$ (100), 235 (6), 219 (20), 207 (22), 193 (21), 175 (12), 161 (26), 147 (32), 133 (8), 125 (8), 105 (7), 97 (7), 91 (13), 83 (75), 77 (11), 72 (58), 67 (14); calcd for $C_{15}H_{22}O_3$ m/e 250.1569, measured m/e 250.1562.

Preparation of 4a from 3-Methoxycyclopent-2-en-1-one. To a solution of LDA prepared at −68 °C in 6 mL of 1:1 THF/hexane from 0.397 g (3.92 mmol) of iPr$_2$NH and 2.45 mL of a 1.6 M solution of nBuLi (3.92 mmol) in hexane was added dropwise over 1 min 0.400 g (3.57 mmol) of 3-methoxycyclopent-1-en-2-one. The mixture was stirred for 30 min at −68 °C, and then 2.195 g (17.85 mmol) of 1-bromopropane in 4 mL of HMPA was added dropwise over 10 min, during which time the temperature rose to −59 °C. The solution was stirred at −62 °C for 3 days, then poured into a saturated aqueous NH_4Cl solution, extracted with EtOAc, and concentrated. The crude reaction mixture was purified on silica gel with EtOAc as eluent to give 0.128 g (23.5%) of the desired cyclopentenone **4a** as a volatile colorless oil which had ^{1}H NMR, ^{13}C NMR, and IR spectra identical to those of **4a** obtained from the reaction of **1c** and 1-pentyne.

Reaction of the Chromium Complex 1c with 3-Methyl-1-butyne. The reaction of 0.104 g (0.41 mmol) of complex **1c**[31] and 0.057 g (0.82 mmol) of 3-methyl-1-butyne in 8 mL of hexane provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.004 g (4%) of **8b** as a bright-yellow waxy semisolid and 0.014 g (23%) of **4b** as a volatile colorless oil. Spectral data for **4b**: ^{1}H NMR ($CDCl_3$) δ 0.79 (d, 3 H, J = 6.8 Hz, iPr-CH_3), 0.83 (d, 3 H, J = 6.7 Hz, iPr-CH_3), 2.25–2.32 (m, 1 H, iPr-CH), 2.36 (d, 1 H, J = 17.3 Hz, 4-CH_{trans}), 2.48–2.53 (m, 1 H, 5-CH), 2.55 (dd, 1 H, J = 17.2, 7.36 Hz, 4-CH_{cis}), 3.82 (s, 3 H, OCH_3), 5.27 (s, 1 H, 2-CH); ^{13}C NMR ($CDCl_3$) δ 16.46 (q, J = 125.0 Hz, iPr-CH_3), 20.66 (q, J = 124.6 Hz, iPr-CH_3), 27.99 (d, J = 130.2 Hz, iPr-CH), 29.94 (t, J = 131.9 Hz, C-4), 51.07 (d, J = 130.1 Hz, C-5), 58.50 (q, J = 146.7 Hz, OCH_3), 104.65 (d, J = 170.5 Hz, C-2), 190.31 (s, C-3), 207.70 (s, C-1); IR (neat) 2958 m, 2932 m, 2872 m, 1692 s, 1597 s, 1465 m, 1357 m, 1245 m, 1192 m, 1164 m, 995 m, 825 m, 733 m cm^{-1}; mass spectrum, m/e (% relative intensity) 154 M$^+$ (10), 139 (8), 112 (100), 97 (15), 83 (13), 77 (3), 69 (12), 65 (2). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.91; H, 9.32. Spectral data for **8b** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 0.91 (d, 6 H, J = 6.9 Hz, iPr-CH_3), 0.94 (d, 6 H, J = 6.9 Hz, iPr-CH_3), 1.80 (s, 3 H, CH_3), 2.05 (sept, 1 H, J = 6.9 Hz, iPr-CH), 2.92 (sept, 1 H, J = 6.8 Hz, iPr-CH), 3.27 (s, 3 H, OCH_3), 4.47 (s, 1 H, 6-CH), 6.77 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$)

(30) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *11*, 819 and references therein.

(31) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 960. (b) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* **1987**, *65*, 140.

δ 16.61 (q, J = 127.4 Hz, iPr-CH_3), 20.74 (q, J = 127.2 Hz, iPr-CH_3 or 7-CH_3), 20.97 (q, J = 127.2 Hz, iPr-CH_3 or 7-CH_3), 25.35 (d, J = 131.9 Hz, iPr-CH), 33.43 (d, J = 131.4 Hz, iPr-CH), 54.35 (q, J = 143.8 Hz, OCH_3), 57.85 (s, C-5), 104.58 (d, J = 163.4 Hz, C-3), 140.16 (dd, J = 170.0, 4.7 Hz, C-6), 153.46 (s, C-2), 169.53 (s, C-7), 206.86 (s, C-1 + C-4); IR (neat) 2965 m, 2936 m, 2875 w, 1740 w, 1697 s, 1673 m, 1614 w, 1466 m, 1382 m, 1371 m, 1312 m, 1262 w, 1244 m, 1216 m, 1150 w, 1097 m, 1062 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 250 M^+ (75), 235 (14), 219 (5), 207 (100), 193 (10), 175 (33), 154 (25), 126 (16), 105 (7), 91 (10), 77 (10), 72 (7), 67 (11); calcd for $C_{15}H_{22}O_3$ *m/e* 250.1569, measured *m/e* 250.1576.

Reaction of the Chromium Complex 1c with 3,3-Dimethyl-1-butyne. The reaction of 0.131 g (0.53 mmol) of complex **1c**[31] and 0.086 g (1.06 mmol) of 3,3-dimethyl-1-butyne in 11 mL of hexane provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.009 g (6%) of **8c** as a bright-yellow waxy semisolid and 0.021 g (23%) of **4c** as a colorless solid (mp = 34–35 °C). Spectral data for **4c**: ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H, tBu-CH_3), 2.30 (dd, 1 H, J = 7.4, 3.1 Hz, 5-CH), 2.42 (ddd, 1 H, J = 17.7, 3.0, 0.8 Hz, 4-CH_{trans}), 2.60 (ddd, 1 H, J = 17.9, 7.7, 0.8 Hz, 4-CH_{cis}), 3.80 (s, 3 H, OCH_3), 5.23 (s, 1 H, 2-CH); ^{13}C NMR ($CDCl_3$) δ 27.37 (q, J = 125.3 Hz, tBu-CH_3), 31.90 (t, J = 130.2 Hz, C-4), 33.05 (s, $C(CH_3)_3$), 54.75 (d, J = 131.3 Hz, C-5), 58.41 (q, J = 146.1 Hz, OCH_3), 105.14 (d, J = 169.5 Hz, C-2), 189.10 (s, C-3), 206.92 (s, C-1); IR (neat) 2956 s, 2907 s, 2869 s, 1692 s, 1603 s, 1462 s, 1351 s, 1258 s, 1190 m, 1165 m, 992 s, 819 m, 734 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 168 M^+ (5), 153 (10), 125 (4), 112 (100), 97 (12), 83 (16), 77 (3), 69 (6), 65 (2); calcd for $C_{10}H_{16}O_2$ *m/e* 168.1150, measured *m/e* 168.1152. Spectral data for **8c** (1 diastereomer, not assigned): ^1H NMR ($CDCl_3$) δ 0.96 (s, 9 H, tBu-CH_3), 1.30 (s, 9 H, tBu-CH_3), 1.82 (s, 3 H, CH_3), 3.25 (s, 3 H, OCH_3), 4.60 (s, 1 H, 6-CH), 6.74 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 16.63 (q, CH_3), 26.37 (q, tBu-CH_3), 28.09 (q, tBu-CH_3), 33.29 (s, $C(CH_3)_3$), 35.74 (s, $C(CH_3)_3$), 54.19 (q, OCH_3), 60.51 (s, C-5), 103.07 (d, C-6), 140.47 (d, C-3), 153.33 (s, C-2), 170.39 (s, C-7), 206.61 (s, C-1 or C-4), 206.97 (s, C-1 or C-4); IR (neat) 2969 s, 2870 m, 1673 s, 1462 m, 1400 m, 1371 m, 1326 m, 1217 m, 1197 m, 1160 m, 1074 m, 913 m, 734 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 278 M^+ (5), 263 (2), 244 (2), 222 (100), 207 (67), 191 (26), 175 (25), 165 (5), 147 (6), 137 (7), 119 (4), 109 (4), 91 (6), 83 (47), 77 (5), 72 (3), 67 (9); calcd for $C_{17}H_{26}O_3$ *m/e* 278.1882, measured *m/e* 278.1881.

A solution of 0.113 g (0.45 mmol) of the trideutereomethyl chromium complex **51**[45] and 0.073 g (0.90 mmol) of 3,3-dimethyl-1-butyne in 9 mL of hexane provided, in order of elution (1:1:10–1:1:4–1:1:1), 0.005 g (4%) of **53** and 0.013 g (17%) of **52**. Spectra data for **52**: ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H, tBu-CH_3), 2.28–2.33 (m, 0.5 H, 5-CH), 2.41 (d, 0.9 H, 4-CH_{trans}), 2.60 (m, 0.5 H, 4-CH_{cis}), 3.80 (s, 3 H, OCH_3), 5.24 (s, 1 H, 2-CH); IR (CCl_4) 2960 m, 2940 m, 2907 w, 2869 w, 2845 w, 1696 s, 1609 w, 1475 w, 1460 w, 1434 w, 1430 w, 1395 w, 1367 m, 1350 m, 1334 s, 1282 w, 1179 w, 1169 w, 1039 w cm^{-1}. Spectral data for **53**: ^1H NMR ($CDCl_3$) δ 0.97 (s, 9 H, tBu-CH_3), 1.31 (s, 9 H, tBu-CH_3), 1.78–1.83 (m, 0.67 H, CH_3), 3.26 (s, 3 H, OCH_3), 4.60 (s, 1 H, 6-CH), 6.74 (s, 1 H, 3-CH); mass spectrum, *m/e* (% relative intensity) 281 M^+ (5), 225 (100), 210 (64), 194 (27), 177 (24), 163 (6), 149 (8), 138 (10), 119 (5), 111 (7), 95 (7), 91 (6), 67 (16).

Reaction of Chromium Complex 1c with 3-Hexyne. The reaction of 0.368 g (1.47 mmol) of complex **1c**[31] and 0.242 g (2.95 mmol) of 3-hexyne in 38 mL of hexane provided, in order of elution (1:1:10–1:1:4–1:1:1), 0.019 g (8%) of **5d**, 0.075 g (30%) of *trans*-**4d**, and 0.011 g (4%) of *cis*-**4d** as colorless oils. Spectral data for *trans*-**4d**: ^1H NMR ($CDCl_3$) δ 0.86 (t, 3 H, J = 7.4 Hz, CH_3), 0.89 (t, 3 H, J = 7.4 Hz, CH_3), 1.47 (m, 2 H, CH_2CH_3), 1.71 (m, 2 H, CH_2CH_3), 2.05 (m, 1 H, 4-CH), 2.41 (m, 1 H, 5-CH), 3.76 (s, 3 H, OCH_3), 5.17 (s, 1 H, 2-CH); ^{13}C NMR ($CDCl_3$) δ 10.57 (q, J = 123.1 Hz, CH_3), 10.99 (q, J = 124.9 Hz, CH_3), 24.40 (t, J = 127.2 Hz, CH_2CH_3), 24.72 (t, J = 128.3 Hz, CH_2CH_3), 46.93 (d, J = 130.6 Hz, C-4), 52.16 (d, J = 130.7 Hz, C-5), 58.47 (q, J = 146.5 Hz, OCH_3), 103.36 (d, J = 169.6 Hz, C-2), 191.94 (s, C-3), 207.32 (s, C-1); IR (CCl_4) 3018 w, 2966 s, 2937 s, 2877 s, 2847 m, 1768 w, 1702 s, 1614 m, 1458 s, 1440 m, 1382 m, 1361 s, 1335 s, 1301 s, 1185 m, 1166 s, 1141 m, 1093 w, 1038 w, 944 w, 908 w cm^{-1}; mass spectrum, *m/e* (relative intensity) 168 M^+ (37), 153 (22), 140 (82), 125 (100), 112 (36), 96 (8), 91 (7), 79 (27), 69 (50); calcd for $C_{10}H_{16}O_2$ *m/e* 168.1150, measured *m/e* 168.1148. The major diastereomer was assigned as trans, since the major diastereomer of **4j** was trans. Spectral data for cis-**4d**: ^1H NMR ($CDCl_3$) δ 0.91 (t, 3 H, J = 7.5 Hz, CH_3), 0.94 (t, 3 H, J = 7.4 Hz, CH_3), 1.52 (m, 2 H, CH_2CH_3), 1.76 (m, 2 H, CH_2CH_3), 2.10 (m, 1 H, 4-CH), 2.46 (m, 1 H, 5-CH), 3.81 (s, 3 H, OCH_3), 5.21 (s, 1 H, 2-CH); IR (CCl_4) 2966 s, 2937 s, 2877 m, 2847 w, 1698 s, 1666 w, 1610 w, 1458 m, 1382 w, 1361 m, 1335 m, 1300 m, 1186 w, 1168 m, 1140 w, 1092 w, 1038 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 168 M^+ (89), 167 (100), 153 (28), 139 (22), 125 (17), 109 (14), 91 (16), 85 (14), 79 (15), 71 (23); calcd for $C_{10}H_{16}O_2$ *m/e* 168.1150, measured *m/e* 168.1155. The minor diastereomer was assigned as cis, since the minor diastereomer of **4j** was cis. Spectral data for **5d**: ^1H NMR ($CDCl_3$) δ 0.99 (t, 3 H, J = 7.6 Hz, Et-CH_3), 1.14 (t, 3 H, J = 7.5 Hz, Et-CH_3), 2.18 (qd, 2 H, J = 7.7, 2.8 Hz, CH_2CH_3), 2.26 (dd, 1 H, J = 18.0, 2.0 Hz, 5-CH_{trans}), 2.41–2.52 (m, 2 H, CH_2CH_3), 2.59 (dd, 1 H, J = 18.0, 5.7 Hz, 5-CH_{cis}), 3.36 (s, 3 H, OCH_3), 4.41 (d, 1 H, J = 5.8 Hz, 4-CH); ^{13}C NMR ($CDCl_3$) δ 12.09 (q, J = 128.3 Hz, CH_3), 13.09 (q, J = 126.7 Hz, CH_3), 16.17 (t, J = 127.6 Hz, CH_2CH_3), 20.88 (t, J = 127.4 Hz, CH_2CH_3), 40.60 (t, J = 131.0 Hz, C-5), 57.09 (q, J = 141.1 Hz, OCH_3), 77.59 (d, J = 142.6 Hz, C-4), 143.56 (s, C-3), 171.29 (s, C-2), 205.29 (s, C-1); IR (CCl_4) 2998 w, 2966 s, 2937 s, 2878 s, 2826 s, 1742 w, 1692 s, 1651 w, 1342 m, 1308 m, 1258 m, 1239 w, 1195 s, 1152 m, 1122 m, 1062 m, 1034 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 168 M^+ (10), 67 (21), 153 (19), 139 (100), 123 (14), 111 (27), 93 (14), 79 (20); calcd for $C_{10}H_{16}O_2$ *m/e* 168.1150, measured *m/e* 168.1147.

Reaction of Chromium Complex 1c with 4-Octyne. The reaction of 0.300 g (1.20 mmol) of complex **1c**[31] and 0.26 g (2.4 mmol) of 4-octyne in 24 mL of hexane provided, in order of elution (1:1:3.5), 0.35 g (20%) of **5e** and 0.67 g (38%) of a 5:2 mixture of *trans*-**4e** and *cis*-**4e** as viscous colorless oils. A 56% total yield of essentially the same ratio of products was obtained when the reaction was run in refluxing 1% aqueous dioxane and 2 equiv of alkyne added via syringe pump over 2 h.[6] Spectral data for *trans* + *cis*-**4e**: ^1H NMR ($CDCl_3$) δ 0.85–0.95 (m, 6 H), 1.25–1.48 (m, 6 H), 1.6–1.8 (m, 2 H), 2.14 (m, 1 H of major isomer), 2.47 (m, 1 H), 2.87 (q, 1 H of minor isomer), 3.79 (s, 3 H of minor isomer), 3.80 (s, 3 H of major isomer), 5.19 (s, 1 H of major isomer), 5.20 (s, 1 H of minor isomer); ^{13}C NMR ($CDCl_3$) δ 14.15, 19.85, 20.11, 20.57, 21.67, 27.56, 30.58, 34.11, 34.58, 43.10, 46.44, 49.71, 51.71, 58.25, 58.50, 102.30, 102.93, 192.16, 192.26, 207.0, 207.58; IR (neat) 3600 w, 3575 w, 2957 s, 2931 s, 2880 m, 1700 s, 1594 s cm^{-1}. The stereochemistry of the major diastereomer was assigned as trans on the basis that the major diastereomer of **4j** was trans. Spectral data for **5e**: ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.4 Hz), 0.96 (t, 3 H, J = 7.4 Hz), 1.41 (m, 2 H), 1.50 (m, 1 H), 1.64 (m, 1 H), 2.1–2.2 (m, 2 H), 2.29 (dd, 1 H, J = 18.0, 1.9 Hz), 2.35–2.5 (m, 2 H), 2.60 (dd, 1 H, J = 18.0, 5.7 Hz), 3.36 (s, 3 H), 4.40 (d, 1 H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.11 (q, J = 124.7 Hz), 14.34 (q, J = 125.8 Hz), 20.78 (t, J = 127.5 Hz), 21.66 (t, J = 127.3 Hz), 24.98 (t, J = 123.3 Hz), 29.80 (t, J = 127.5 Hz), 40.56 (t, J = 131.4 Hz), 57.00 (q, J = 141.2 Hz), 77.69 (d, J = 139.6 Hz), 142.7 (s), 170.5 (s), 205.4 (s); IR (neat) 3609 w, 3583 w, 2691 s, 2929 s, 2872 m, 1709 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 196 M^+ (31), 181 (13), 164 (10), 153 (100), 125 (13), 79 (12); calcd for $C_{12}H_{20}O_2$ *m/e* 196.1463, measured *m/e* 196.1460.

Reaction of Chromium Complex 1c with 6-Dodecyne. The reaction of 0.652 g (2.60 mmol) of complex **1c**[31] and 0.825 g (5.20 mmol) of 6-dodecyne in 40 mL of hexane provided, in order of elution (1:1:10–1:1:4–1:1:1), 0.154 g (23%) of **5f** and 0.227 g (35%) of *trans*-**4f** as viscous colorless oils. Spectral data for *trans*-**4f**: ^1H NMR ($CDCl_3$) δ 0.71–0.94 (m, 6 H, CH_3), 1.26 (br s, 12 H, CH_2), 1.32–1.48 (m, 2 H, CH_2), 1.59–1.77 (m, 2 H, CH_2), 2.08–2.13 (m, 1 H, 4-CH), 2.40–2.48 (m, 1 H, 5-CH), 3.78 (s, 3 H, OCH_3), 5.17 (s, 1 H, 2-CH); ^{13}C NMR ($CDCl_3$) δ 14.35 (q, J = 124.5 Hz, CH_3), 14.38 (q, J = 124.5 Hz, CH_3), 22.83 (t, J = 126.0 Hz, CH_2), 26.56 (t, J = 124.3 Hz, CH_2), 26.85 (t, J = 123.4 Hz, CH_2), 32.22 (t, CH_2), 32.26 (t, J = 127.9 Hz, CH_2), 32.31 (t, J = 128.7 Hz, CH_2), 32.41 (t, CH_2), 32.61 (t, J = 126.3 Hz, CH_2), 46.89 (d, J = 129.4 Hz, C-4), 52.17 (d, J = 130.7 Hz, C-5), 58.92 (q, J = 146.4 Hz, OCH_3), 103.43 (d, J = 164.8 Hz, C-2), 192.63 (s, C-3), 207.91 (s, C-1); IR (CCl_4) 3018 w, 2962 m, 2913 m, 2845 w, 1699 s, 1610 w, 1487 m, 1460 m, 1454 m, 1439 m, 1356 s, 1343 s, 1310 m, 1294 m, 1188 w, 1166 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 252 M^+ (5), 196 (3), 195 (20), 182 (30), 137 (4), 125 (100), 112 (47), 97 (58), 91 (5), 79 (7). Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.50; H, 11.24. The stereochemistry was assigned as trans, since the major diastereomer of **4j** was trans. Spectral data for **5f**: ^1H NMR ($CDCl_3$) δ 0.86 (t, 3 H, J = 7.1 Hz, CH_3), 0.91 (t, 3 H, J = 7.0 Hz, CH_3), 1.14–1.47 (m, 10 H, CH_2), 1.38–1.52 (m, 1 H), 1.52–1.66 (m, 1 H), 2.07–2.21 (m, 2 H), 2.26 (d, 1 H, J = 18.0 Hz, 5-CH_{trans}), 2.35–2.49 (m, 2 H), 2.59 (dd, 1 H, J = 18, 5.9 Hz, 5-CH_{cis}), 3.36 (s, 3 H, OCH_3), 4.38 (d, 1 H, J = 4.9 Hz, 4-CH); ^{13}C NMR ($CDCl_3$) δ 14.34 (q, J = 123.9 Hz, CH_3), 14.38 (q, J = 124.3 Hz, CH_3), 22.85 (t, J = 126.3 Hz, 2 CH_2 carbons), 23.43 (t, J = 124.5 Hz, CH_2), 27.57 (t, J = 126.5 Hz, CH_2), 28.16 (t, J = 127.4 Hz, CH_2), 28.55 (t, J = 126.9 Hz, CH_2), 32.27 (t, J = 129.0 Hz, CH_2), 32.42 (t, J = 122.2 Hz, CH_2), 41.02 (t, J = 132.0 Hz, CH_2), 57.42 (q, J = 141.3 Hz, OCH_3), 78.17 (d, J = 140.1 Hz, C-4), 143.17 (s, C-3), 171.06 (s, C-2), 205.78 (s, C-1); IR (CCl_4) 2996 w, 2942 w, 2916 m, 2822 m, 1711 s, 1648 m, 1467 m, 1462 m, 1440 w, 1405 w, 1378 w, 1359 m, 1344 m, 1303 w, 1191 w, 1177 w, 1095 m, 1047 w cm^{-1}; mass spectrum, *m/e* (relative intensity) 252 M^+

(31), 220 (20), 209 (24), 193 (4), 181 (100), 165 (5), 153 (12), 149 (7), 139 (5), 135 (5), 125 (8), 121 (6), 110 (13), 105 (4), 97 (6), 93 (10), 87 (4), 79 (17). Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.10; H, 11.23.

Reaction of Chromium Complex 1c with 7-Tetradecyne. The reaction of 0.873 g (3.50 mmol) of complex **1c**[31] and 1.302 g (7.00 mmol) of 7-tetradecyne in 70 mL of hexane provided, in order of elution (1:1:10–1:1:4–1:1:1), 0.201 g (21%) of **5g** and 0.289 g (29%) of a 4.2:1 mixture of *trans*-**4g** and *cis*-**4g** as viscous colorless oils. Spectral data for *trans*-**4g**: ^{1}H NMR ($CDCl_3$) δ 0.65–0.85 (m, 6 H, CH_3), 1.00–1.30 (m, 16 H, CH_2), 1.24–1.41 (m, 2 H, CH_2), 1.52–1.70 (m, 2 H, CH_2), 1.98–2.05 (m, 1 H, 4-CH), 2.32–2.40 (m, 1 H, 5-CH), 3.70 (s, 3 H, OCH_3), 5.08 (s, 1 H, 2-CH); ^{13}C NMR ($CDCl_3$) δ 14.36 (q, J = 124.1 Hz, 2 CH_3 carbons), 22.92 (t, J = 124.0 Hz, CH_2), 26.80 (t, J = 124.5 Hz, CH_2), 27.11 (t, J = 121.4 Hz, CH_2), 29.72 (t, J = 123.9 Hz, CH_2), 29.75 (t, J = 125.7 Hz, CH_2), 32.00 (t, J = 125.6 Hz, 2-CH_2 carbons), 32.22 (t, J = 127.7 Hz, CH_2), 32.64 (t, J = 127.4 Hz, CH_2), 46.85 (d, J = 125.9 Hz, C-4), 52.10 (d, J = 130.2 Hz, C-5), 58.86 (q, J = 146.1 Hz, OCH_3), 103.37 (d, J = 169.6 Hz, C-2), 192.50 (s, C-3), 207.65 (s, C-1), 1 carbon not found; IR (CCl_4) 2958 s, 2931 s, 2873 m, 2858 s, 1720 w, 1702 s, 1697 s, 1695 s, 1673 w, 1618 w, 1607 w, 1467 w, 1461 m, 1454 m, 1446 w, 1439 w, 1378 w, 1352 m, 1310 w, 1187 w, 1166 m, 909 w cm^{-1}; mass spectrum, m/e (% relative intensity) 280 M^+ (15), 209 (47), 196 (88), 167 (3), 137 (4), 125 (100), 112 (76), 97 (4), 79 (6). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 77.34; H, 11.62. The stereochemistry of the major isomer was assigned as trans on the basis that the major diastereomer of **4j** was trans. Spectral data for *cis*-**4g**: (characteristic ^{1}H NMR signals extracted from mixture of cis and trans isomers, 500 MHz, $CDCl_3$) δ 2.72–2.79 (m, 1 H, 4-CH or 5-CH), 3.68 (s, 3 H, OCH_3), 5.09 (s, 1 H, 2-CH). Spectral data for **5g**: ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3 H, CH_3), 0.85 (t, 3 H, CH_3), 1.07–1.40 (m, 14 H, CH_2), 1.33–1.46 (m, 1 H), 1.40–1.60 (m, 1 H), 2.05–2.18 (m, 2 H), 2.21 (dd, 1 H, J = 18.02, 1.95 Hz, 5-CH_{trans}), 2.32–2.45 (m, 2 H), 2.55 (dd, 1 H, J = 18.01, 5.85 Hz, 5-CH_{cis}), 3.32 (s, 3 H, OCH_3), 4.35 (d, 1 H, J = 5.24 Hz, 4-CH); ^{13}C NMR ($CDCl_3$) δ 14.43 (q, J = 123.3 Hz, 2 CH_3 carbons), 22.94 (t, J = 126.1 Hz, CH_2), 23.45 (t, J = 128.1 Hz, CH_2), 27.84 (t, CH_2), 27.89 (t, CH_2), 28.18 (t, J = 126.1 Hz, CH_2), 28.80 (t, CH_2), 29.76 (t, J = 129.3 Hz, CH_2), 29.93 (t, J = 127.0 Hz, CH_2), 31.98 (t, J = 128.4 Hz, 2 CH_2 carbons), 40.97 (t, J = 130.5 Hz, CH_2), 57.36 (q, J = 141.3 Hz, OCH_3), 78.15 (d, J = 141.3 Hz, C-4), 143.11 (s, C-3), 170.99 (s, C-2), 205.67 (s, C-1); IR (CCl_4) 2957 s, 2931 s, 2873 m, 2859 s, 2822 w, 1709 s, 1655 w, 1649 w, 1644 w, 1460 w, 1451 w, 1447 w, 1406 w, 1379 w, 1361 w, 1345 m, 1303 w, 1190 w, 1171 w, 1099 m, 1049 w, 909 w cm^{-1}; mass spectrum, m/e (% relative intensity) 280 M^+ (25), 248 (14), 223 (20), 209 (3), 195 (100), 179 (3), 165 (7), 153 (4), 125 (7), 121 (4), 110 (10), 93 (8), 79 (13). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.40; H, 11.43.

Reaction of Chromium Complex 1c with 8-Hexadecyne. The reaction of 0.700 g (2.80 mmol) of complex **1c**[31] and 1.201 g (5.60 mmol) of 8-hexadecyne in 56 mL of hexane provided, in order of elution (1:1:4), 0.164 g (19%) of **5h** and 0.277 g (29%) of a 5.6:1 mixture of *trans*-**4h** and *cis*-**4h** as viscous colorless oils. Spectral data for *trans*-**4h**: ^{1}H NMR ($CDCl_3$) δ 0.78–0.94 (m, 6 H, CH_3), 1.08–1.42 (m, 20 H, CH_2), 1.35–1.52 (m, 2 H, CH_2), 1.64–1.77 (m, 2 H, CH_2), 2.10–2.16 (m, 1 H, 4-CH), 2.43–2.50 (m, 1 H, 5-CH), 3.80 (s, 3 H, OCH_3), 5.19 (s, 1 H, 2-CH); ^{13}C NMR ($CDCl_3$) δ 14.40 (q, J = 124.4 Hz, 2 CH_3 carbons), 22.97 (t, J = 124.3 Hz, 2 CH_2 carbons), 26.87 (t, J = 124.6 Hz, CH_2), 27.20 (t, J = 125.4 Hz, CH_2), 29.47 (t, J = 125.5 Hz, 2 CH_2 carbons), 30.03 (t, CH_2), 30.08 (t, J = 123.6 Hz, CH_2), 32.14 (t, CH_2), 32.16 (t, CH_2), 32.25 (t, J = 127.3 Hz, CH_2), 32.65 (t, J = 126.6 Hz, CH_2), 46.87 (d, J = 130.3 Hz, C-4), 52.14 (d, J = 131.5 Hz, C-5), 58.87 (q, J = 146.10 Hz, OCH_3), 103.40 (d, J = 168.2 Hz, C-2), 192.55 (s, C-3), 207.77 (s, C-1); IR (CCl_4) 3018 w, 2957 s, 2927 s, 2873 m, 2857 s, 1719 w, 1707 s, 1703 s, 1693 s, 1683 m, 1673 w, 1660 w, 1618 w, 1608 w, 1467 m, 1460 m, 1454 m, 1446 w, 1439 m, 1377 m, 1352 s, 1310 m, 1187 w, 1166 s cm^{-1}; mass spectrum, m/e (% relative intensity) 308 M^+ (8), 223 (26), 210 (52), 195 (4), 167 (3), 137 (5), 125 (100), 112 (51), 97 (4), 91 (3), 83 (32), 79 (5). Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.87; H, 11.76. Found: C, 78.00; H, 11.87. The stereochemistry of the major isomer was assigned as trans on the basis that the major diastereomer of **4j** was trans. Spectral data *cis*-**4h**: (characteristic ^{1}H NMR signals extracted from the mixture of cis and trans isomers, 500 MHz, $CDCl_3$) δ 2.83–2.89 (m, 1 H, 4-CH or 5-CH), 3.79 (s, 3 H, OCH_3), 5.20 (s, 1 H, 2-CH). Spectral data for **5h**: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3 H, J = 7.06 Hz, CH_3), 0.90 (t, 3 H, J = 6.55 Hz, CH_3), 1.16–1.43 (m, 18 H, CH_2), 1.40–1.50 (m, 1 H), 1.53–1.65 (m, 1 H), 2.09–2.22 (m, 2 H), 2.27 (dd, 1 H, J = 17.99, 1.85 Hz, 5-CH_{trans}), 2.38–2.50 (m, 2 H), 2.60 (dd, 1 H, J = 17.98, 5.80 Hz, 5-CH_{cis}), 3.37 (s, 3 H, OCH_3), 4.40 (d, 1 H, J = 5.27 Hz, 4-CH); ^{13}C NMR ($CDCl_3$) δ 14.46 (q, J = 124.3 Hz, 2 CH_3 carbons), 23.03 (t, J = 126.2 Hz, 2 CH_2 carbons), 23.46 (t, J = 127.5 Hz, CH_2), 27.88 (t, J = 125.7 Hz, CH_2), 27.94 (t, J = 127.1 Hz, CH_2), 28.18 (t, CH_2), 28.85 (t, J = 126.8 Hz, CH_2), 29.46 (t, J = 126.5 Hz, CH_2), 30.07 (t, J = 121.9 Hz, CH_2), 30.22 (t, J = 121.2 Hz, CH_2), 32.12 (t, J = 126.2 Hz, CH_2), 32.17 (t, CH_2), 40.98 (t, J = 131.5 Hz, CH_2), 57.36 (q, J = 141.5 Hz, OCH_3), 78.16 (d, J = 152.2 Hz, C-4), 143.13 (s, C-3), 170.99 (s, C-2), 205.67 (s, C-1); IR (CCl_4) 2956 s, 2928 s, 2873 m, 2857 s, 2822 w, 1736 w, 1711 s, 1698 m, 1655 w, 1649 m, 1640 m, 1633 w, 1466 m, 1462 m, 1454 m, 1446 w, 1435 w, 1406 w, 1379 m, 1364 m, 1345 s, 1302 m, 1189 w, 1155 w, 1099 m, 1049 w cm^{-1}; mass spectrum, m/e (% relative intensity) 308 M^+ (25), 276 (8), 252 (3), 237 (15), 223 (3), 209 (80), 193 (3), 179 (5), 153 (4), 135 (3), 125 (7), 118 (3), 110 (8), 93, 83 (100), 79 (8). Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.87; H, 11.76. Found: C, 78.12; H, 11.88.

Reaction of Chromium Complex 1c with Enyne 25. A solution of 0.122 g (0.49 mmol) of complex **1c**[31] and 0.089 g (0.73 mmol) of enyne **25**[32] in 108 mL of hexane provided (after column chromatography on triethylamine-treated silica gel), in order of elution, 0.015 g (14%) of **14i** as a pale-yellow oil and 0.053 g (52%) of **4i** as a pale-yellow oil. Spectral data for **4i** (1:1 mixture of diastereomers): ^{1}H NMR ($CDCl_3$) isomer A, δ 0.95 (d, 3 H, J = 6.8 Hz), 1.19–1.26 (m, 1 H), 1.36–1.49 (m, 1 H), 1.68 (s, 3 H), 1.91–2.20 (m, 3 H), 2.37 (dd, 1 H, J = 17.6, 2.4 Hz), 2.51–2.63 (m, 2 H), 3.82 (s, 3 H), 4.63 (s, 1 H), 4.66 (s, 1 H), 5.27 (s, 1 H); isomer B, δ 0.75 (d, 3 H, J = 6.7 Hz), 1.19–1.26 (m, 1 H), 1.36–1.49 (m, 1 H), 1.71 (s, 3 H), 1.91–2.10 (m, 3 H), 2.37 (dd, 1 H, J = 17.6, 2.4 Hz), 2.51–2.63 (m, 2 H), 3.81 (s, 3 H), 4.66 (s, 1 H), 4.68 (s, 1 H), 5.28 (s, 1 H); ^{13}C NMR ($CDCl_3$) isomer A, δ 13.7, 22.2, 29.5, 32.2, 33.1, 35.5, 50.8, 58.5, 104.8, 109.9, 145.6, 190.4, 207.8; isomer B, δ 17.1, 22.4, 29.3, 31.0, 32.9, 35.5, 49.4, 58.5, 104.9, 109.8, 145.8, 190.1, 207.4; IR ($CHCl_3$) 2875–2977 m, br, 2242 w, 1683 m, 1596 s, 1358 m, 1246 w, 1169 w, 1112 m cm^{-1}; mass spectrum, m/e (% relative intensity) 208 M^+ (21), 193 (15), 179 (5), 165 (4), 153 (20), 139 (100), 125 (74), 112 (100), 97 (70), 91 (19), 83 (43), 77 (32), 69 (64); calcd for $C_{13}H_{20}O_2$ m/e 208.1463, measured m/e 208.1459. Spectral data for **14i**: ^{1}H ($CDCl_3$) δ 1.12 (d, 3 H, J = 6.89 Hz), 1.41–1.50 (m, 1 H), 1.62~1.74 (m, 2 H), 1.68 (s, 3 H), 2.01 (t, 2 H, J = 7.75 Hz), 2.21 (s, 3 H), 3.79 (s, 3 H), 4.65 (s, 1 H), 4.70 (s, 1 H), 6.10 (s, 1 H); ^{13}C ($CDCl_3$) δ 18.70, 22.25, 30.24, 32.59, 35.08, 37.98, 52.16, 110.33, 126.18, 145.05, 152.34, 169.33, 196.84; IR (neat) 2950–2930 s, 2874–2839 m, 1734 s, 1700 s, 1619 s, 1455 m, 1435 m, 1375 m, 1246 s, 1175 s, 887 m cm^{-1}; mass spectrum, m/e (% relative intensity) 224 M^+ (3), 208 (6), 193 (13), 181 (20), 165 (60), 156 (43), 149 (27), 139 (22), 124 (100), 112 (46), 107 (55), 96 (55), 79 (24), 69 (30); calcd for $C_{13}H_{20}O_3$ m/e 224.1441, measured m/e 224.1422.

Reaction of Chromium Complex 1c with Diphenylacetylene. The reaction of 0.266 g (1.06 mmol) of complex **1c**[31] and 0.208 g (1.17 mmol) of diphenylacetylene in 18 mL of hexane provided (after oxidation with 3.8 g, 7 equiv, of $[Fe(DMF)_3Cl_2][FeCl_4]$ complex[33]), in order of elution (1:1:10–1:1:4–1:1:1), 0.031 g (7%) of **15j** as a white solid, 0.031 g (11%) of **9j**, 0.024 g (9%) of **5j**, 0.026 g (9%) of *trans*-**4j**, and 0.012 g (4%) of *cis*-**4j**. Spectral data for *trans*-**4j**: mp = 105 °C; ^{1}H NMR ($CDCl_3$) δ 3.62 (br s, 1 H, 4-CH), 3.88 (s, 3 H, OCH_3), 4.01 (br s, 1 H, 5-CH), 5.59 (s, 1 H, 2-CH), 7.10–7.40 (m, 10 H, aryl CH); ^{13}C NMR ($CDCl_3$) δ 56.46 (d, J = 132.9 Hz, C-4 or C-5), 59.13 (q, J = 147.4 Hz, OCH_3), 62.45 (d, J = 132.0 Hz, C-4 or C-5), 104.58 (d, J = 170.4 Hz, C-2), 127.13 (d, aryl C-4), 127.25 (d, aryl CH), 127.48 (d, aryl C-4), 127.69 (daryl CH), 128.82 (d, aryl CH), 128.95 (d, aryl CH), 138.77 (s, aryl C-1), 139.29 (s, aryl C-1), 190.16 (s, C-3), 203.92 (s, C-1); IR (CCl_4) 2978 s, 2936 w, 2927 w, 2897 w, 2868 m, 1705 s, 1604 s, 1454 w, 1382 w, 1351 m, 1331 m, 1165 m, 1120 s, 1078 w, 1044 w, 909 w, 696 w cm^{-1}; mass spectrum, m/e (% relative intensity) 264 M^+ (100), 249 (5), 235 (26), 220 (8), 205 (28), 187 (23), 178 (22), 159 (15), 152 (5), 145 (6), 128 (9), 115 (16), 105 (15), 91 (29), 84 (7), 77 (16), 69 (37); calcd for $C_{18}H_{16}O_2$ m/e 264.1150, measured m/e 264.1158. The stereochemical assignment of trans was made by comparison with the spectral data previously reported for *trans*-**4j**.[6a] Spectral data for *cis*-**4j**: ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3 H, OCH_3), 4.26 (d, 1 H, J = 7.9 Hz, 4-CH), 4.49 (d, 1 H, J = 7.9 Hz, 5-CH), 5.75 (s, 1 H, 2-CH), 6.76–6.82 (m, 4 H, aryl CH), 6.91–7.04 (m, 6 H, aryl CH); ^{13}C NMR ($CDCl_3$) δ 52.95, 58.15, 59.00, 106.34 (d, C-2), 126.47 (d, aryl C-4), 126.93 (d, aryl C-4), 127.77 (d, aryl CH), 128.01 (d, aryl CH), 128.90 (d, aryl CH), 130.10 (d, aryl CH), 135.83 (s, aryl C-1), 136.40 (s, aryl C-1), 189.54 (s, C-3), 204.87 (s, C-1); IR (CCl_4) 2977 m, 2925 m, 2869 m, 1705 s, 1607 m, 1455 w, 1439 w, 1381 w, 1351 m, 1332 m, 1165 m, 1154 m, 1121 m, 1099 w, 1043 w, 1036 w, 909 m, cm^{-1}; mass spectrum, m/e (% relative intensity) 264 M^+ (100), 249 (18), 233 (41), 220 (14), 205 (27), 187 (60), 178 (33), 165 (22), 159 (37), 149 (28), 139 (20), 123 (37), 115 (38), 105 (26), 95 (24), 91 (58), 85 (19), 81 (27), 77 (38), 73 (55), 69

(32) Wulff, W. D.; Kim, O. K. Unpublished results.
(33) Tobinaga, S.; Kotani, E. *J. Am. Chem. Soc.* **1972**, *94*, 309.

(88); calcd for $C_{18}H_{16}O_2$ m/e 264.1150, measured m/e 264.1143. The stereochemical assignment of cis was made by comparison with the spectral data previously reported for *cis*-**4j**.[6a] Spectral data for **5j**: mp = 116 °C; ^{1}H NMR ($CDCl_3$) δ 2.70 (d, 1 H, J = 18.2 Hz, 5-CH_{trans}), 2.98 (dd, 1 H, J = 18.2, 6.0 Hz, 5-CH_{cis}), 3.42 (s, 3 H, OCH_3), 5.06 (d, 1 H, J = 5.9 Hz, 4-CH), 7.16–7.38 (m, 10 H, aryl-CH); ^{13}C NMR ($CDCl_3$) δ 41.06 (t, C-5), 56.82 (q, OCH_3), 77.93 (d, C-4), 128.24 (d, aryl CH), 128.39 (d, aryl CH), 128.85 (d, aryl CH), 129.53 (d, aryl CH), 129.70 (D, aryl CH), 131.12 (s, aryl C-1), 133.68 (s, aryl C-1), 141.3 (s, C-2), 165.2 (s, C-3), 203.3 (s, C-1), 1 carbon not located; IR (CCl_4) 2978 s, 2935 m, 2897 m, 2867 s, 1714 m, 1443 w, 1382 m, 1350 m, 1152 m, 1121 s, 1078 w, 909 s cm^{-1}; mass spectrum, m/e (relative intensity) 264 M$^+$ (100), 249 (3), 233 (54), 221 (12), 205 (54), 194 (6), 187 (16), 178 (37), 165 (6), 152 (7), 145 (3), 121 (20), 103 (18), 91 (21), 85 (4), 77 (15), 71 (3), 65 (3); calcd for $C_{18}H_{16}O_2$ m/e 264.1150, measured m/e 264.1148. Spectral data for **9j**: ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3 H, CH_3), 3.39 (s, 3 H, OCH_3), 7.34–7.52 (m, 6 H, aryl CH), 7.74 (d, 2 H, J = 7.0 Hz, aryl CH), 7.85 (d, 2 H, J = 7.2 Hz, aryl CH); IR (CCl_4) 3069 w, 2985 w, 2991 w, 2828 w, 1757 s, 1624 w, 1444 w, 1344 m, 1144 m, 1088 w, 1064 w, 908 w, 690 w, 639 w cm^{-1}. These spectral data were found to be identical to those of a product previously reported for this reaction.[8] Spectral data for the 1.4:1 mixture of isomers of **15j**: mp = 89–91 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 3.19 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 4.21 (s, 1 H, cyclopentenyl-CH), 4.28 (s, 1 H, cyclopentenyl-CH), 6.92–7.32 (m, 38 H, aryl-CH); IR (CCl_4) 3085 w, 3064 w, 3030 m, 2991 m, 2941 m, 2907 w, 2869 w, 2835 w, 1634 s, 1441 m, 1380 m, 1307 m, 1159 s, 1128 s, 1077 m, 1051 s, 908 m, 692 w cm^{-1}; mass spectrum, m/e (% relative intensity) 414 M$^+$ (83), 398 (5), 384 (10), 358 (25), 305 (7), 267 (35), 252 (7), 237 (8), 207 (18), 192 (30), 179 (22), 165 (16), 147 (20), 122 (13), 105 (100), 91 (16), 77 (42), 69 (21); calcd for $C_{31}H_{26}O$ m/e 414.1984, measured m/e 414.1996.

Reaction in *n*-butyl ether at high concentration:[8] The reaction of 0.224 g (0.90 mmol) of complex **1c**[31] and 0.174 g (0.98 mmol) of diphenylacetylene in 2.4 mL of nBu_2O provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.010 g (4%) of **13j** as a white solid, 0.030 g (13%) of **9j** as a pale-yellow solid, 0.014 g (4%) of chromium tricarbonyl complexed **9j** as a bright-red solid, 0.012 g (5%) of **5j** as a white solid, and 0.023 g (10%) of *trans*-**4j** as a white solid. When the crude reaction mixture was oxidized with $[Fe(DMF)_3Cl_2][FeCl_4]$,[33] the yields of **9j**, **14j**, **5j**, and *trans*-**4j** were 25, 6, 3, and 6%, respectively. Oxidation of the crude reaction mixture with 0.5 M aqueous cerium ammonium nitrate (CAN) provided **9j** in 15% yield, **5j** in 4% yield, and *trans*-**4j** in 9% yield. Spectral data for **13j**: ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3 H, CH_3), 3.94 (s, 3 H, OCH_3), 7.09–7.29 (m, 10 H); IR (CCl_4) 3061 w, 2944 w, 1636 w, 1614 m, 1445 w, 1394 w, 1380 m, 1330 m, 1203 w, 1174 w, 1045 w, 1026 w, 908 vs, 699 m cm^{-1}; mass spectrum, m/e (% relative intensity) 264 M$^+$ (100), 249 (65), 238 (3), 230 (2), 221 (2), 202 (9), 191 (5), 178 (37), 165 (5), 152 (12), 139 (3), 126 (6), 115 (6), 102 (4), 83 (10), 77 (12), 65 (3). Spectral data for **14j**: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H, CH_3), 3.78 (s, 3 H, OCH_3), 7.039 (d, 2 H, J = 7.81 Hz, aryl 2+6-CH), 7.042 (d, 2 H, J = 7.47 Hz, aryl 2+6-CH), 7.13–7.12 (m, 6 H, aryl CH); ^{13}C NMR ($CDCl_3$) δ 29.28 (q, CH_3), 52.63 (q, OCH_3), 128.08 (d, aryl CH), 128.57 (d, aryl CH), 129.29 (d, aryl CH), 130.09 (d, aryl CH), 133.46 (s, aryl C-1), 134.00 (s, aryl C-1), 150.52 (s, C-2 or C-3), 168.61 (s, C-1), 203.02 (s, C-4), 3 aryl carbons not located; IR (CCl_4) 3063 w, 3021 w, 2951 w, 1720 s, 1710 s, 1444 m, 1434 m, 1383 w, 1349 m, 1316 w, 1300 m, 1165 m, 1050 m, 910 m, 695 w cm^{-1}; mass spectrum, m/e (% relative intensity) 280 M$^+$ (18), 265 (10), 248 (71), 237 (9), 220 (20), 207 (44), 192 (28), 178 (100), 165 (9), 152 (15), 139 (5), 121 (9), 115 (10), 105 (7), 89 (10), 76 (9); calcd for $C_{18}H_{16}O_3$ m/e 280.1099, measured m/e 280.1098.

Reaction in *n*-butyl ether at low concentration: The reaction of 0.215 g (0.86 mmol) of complex **1c**[31] and 0.345 g (1.93 mmol) of diphenylacetylene in 17 mL of nBu_2O provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.023 g (10%) of **9j**, 0.012 g (13%) of **5j**, and 0.069 g (23%) of a 2:1 mixture of *trans*-**4j** and *cis*-**4j**.

Reaction of Chromium Complex 1c with Phenylacetylene. The reaction of 0.344 g (1.38 mmol) of complex **1c**[31] and 0.281 g (2.76 mmol) of phenylacetylene in 28 mL of hexane provided, in order of elution (1:1:30–1:1:10–1:1:4-Et_2O), 0.137 g (34%) of a 1.8:1 mixture of **10k** and **11k** and 0.017 g (7%) of **4k**. Spectral data for **4k**: ^{1}H NMR ($CDCl_3$) δ 2.74 (dd, 1 H, J = 17.95, 3.08 Hz, 4-CH_{cis}), 3.70 (dd, 1 H, J = 7.79, 3.04 Hz, 5-CH), 3.13 (dd, 1 H, J = 17.83, 7.40 Hz, 4-CH_{trans}), 3.91 (s, 3 H, OCH_3), 5.39 (s, 1 H, 2-CH), 7.16 (d, 2 H, J = 7.78 Hz, aryl 2+6-CH), 7.22 (t, 1 H, J = 8.55 Hz, aryl 4-CH), 7.30 (t, 2 H, J = 7.25 Hz, aryl 3+5-CH); ^{13}C NMR ($CDCl_3$) δ 37.72 (t, C-4), 51.42 (d, C-5), 58.85 (q, OCH_3), 103.66 (d, C-2), 127.03 (d, aryl C-4), 127.55 (d, aryl C-2+6 or C-3+5), 128.82 (d, aryl C-2+6 or C-3+5), 190.12 (s, C-3), 204.97 (s, C-1), 1 aryl carbon not located; IR (CCl_4) 2978 w, 2940 w, 2868 w, 1704 s, 1608 w, 1455 w, 1448 w, 1431 w, 1351 s, 1165 m, 1121 w, 908 m cm^{-1}; mass spectrum, m/e (% relative intensity) 188 M$^+$ (100), 173 (21), 159 (44), 155 (9), 145 (16), 128 (27), 115 (18), 111 (19), 103 (12), 91 (18), 77 (11), 69 (58); calcd for $C_{12}H_{12}O_2$ m/e 188.0837, measured m/e 188.0832. Spectral data for the mixture of **10k** + **11k**: ^{1}H NMR ($CDCl_3$) δ 1.91 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 5.32 (s, 1 H, OH), 5.81 (s, 1 H), 5.88 (s, 1 H), 7.20–7.60 (m, 24 H, aryl CH), 8.00 (m, 1 H, aryl CH), 8.32 (m, 1 H, aryl CH); IR (CCl_4) 3561 s, 3083 s, 3063 m, 3032 m, 2978 m, 2957 m, 2866 m, 1471 s, 1457 m, 1431 s, 1350 m, 1321 m, 1311 m, 1173 m, 1157 m, 1124 m, 1096 m, 1049 m, 908 m cm^{-1}. These spectral data were found to be identical to those reported previously for **10k** and **11k**.[8,9]

Reaction of Chromium Complex 1c with 1-Phenyl-1-propyne. The reaction of 0.419 g (1.68 mmol) of complex **1c**[31] and 0.272 g (2.35 mmol) of 1-phenyl-1-propyne in 21 mL of THF provided, in order of elution (1:1:4), 0.027 g (8%) of **9l**, 0.086 g (26%) of **5l**, and 0.046 g (14%) of a 2.7:1 mixture of *trans*-**4l** and *cis*-**4l**. Spectral data for *trans*-**4l**: ^{1}H NMR ($CDCl_3$) δ 1.32 (d, 3 H, J = 7.1 Hz), 2.90 (dd, 1 H, J = 7.1, 3.1 Hz), 3.22 (d, 1 H, J = 3.2 Hz), 3.89 (s, 3 H), 5.34 (s, 1 H), 7.13 (d, 2 H, J = 7.3 Hz), 7.22 (t, 1 H, J = 7.3 Hz), 7.29 (t, 2 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 17.02, 44.98, 58.84, 60.80, 102.62, 126.93, 127.77, 128.69, 139.04, 192.62, 203.95; IR (neat) 3027 m, 2969 m, 2938 m, 1696 s, 1593 s, 1496 m, 1454 m, 1378 m, 1350 s, 1298 m, 1236 m, 1167 s, 985 m, 757 m, 698 m cm^{-1}; mass spectrum, m/e (% relative intensity) 202 M$^+$ (100), 187 (62), 173 (22), 159 (15), 144 (8), 143 (7), 141 (10), 128 (17), 127 (12), 125 (20); calcd for $C_{13}H_{14}O_2$ m/e 202.0994, measured m/e 202.1004. The stereochemistry of the major isomer was assigned as trans on the basis that the major diastereomer of **4j** was trans. Spectral data for *cis*-**4l**: ^{1}H NMR ($CDCl_3$) δ 0.77 (d, 3 H, J = 7.4 Hz), 3.18–3.24 (m, 1 H), 3.89 (s, 3 H), 3.93 (d, 1 H, J = 7.6 Hz), 5.44 (s, 1 H), 7.05 (d, 2 H, J = 7.4 Hz), 7.20–7.30 (m, 3 H); IR (neat) 3029 w, 2975 m, 2936 m, 1695 s, 1593 s, 1496 m, 1457 m, 1378 m, 1348 s, 1242 s, 1168 m, 984 m, 821 m, 759 m, 720 m cm^{-1}. Spectral data for **5l**: ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3 H), 2.47 (d, 1 H, J = 18.2 Hz), 2.79 (dd, 1 H, J = 18.2, 6.0 Hz), 3.46 (s, 3 H), 4.43 (d, 1 H, J = 5.5 Hz), 7.27–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.97, 40.96, 57.31, 79.63, 128.03, 128.22, 129.08, 130.57, 141.69, 168.18, 203.16; IR (neat) 2983 m, 2931 m, 2824 m, 1704 s, 1642 m, 1496 m, 1445 m, 1378 s, 1345 s, 1302 m, 1195 s, 1138 m, 1099 s, 979 m, 768 m, 699 s cm^{-1}; mass spectrum, m/e (% relative intensity) 202 M$^+$ (65), 187 (100), 174 (18), 171 (17), 159 (24), 155 (15), 143 (32), 142 (14), 140 (22), 129 (20), 128 (50); calcd for $C_{13}H_{14}O_2$ m/e 202.0994, measured m/e 202.1003. Spectral data for **9l**: ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 3 H), 2.43 (s, 3 H), 3.30 (s, 3 H), 7.34 (t, 1 H, J = 7.2 Hz), 7.40 (t, 2 H, J = 7.4 Hz), 7.71 (d, 2 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 12.52, 18.18, 15.84, 86.33, 96.70, 127.60, 128.77, 129.25, 146.07, 176.86, 194.74; IR (neat) 2930 m, 1756 s, 1704 m, 1591 m, 1448 m, 1330 m, 1143 s, 1066 m, 789 m, 697 s cm^{-1}; mass spectrum, m/e (relative intensity) 202 M$^+$ (100), 187 (48), 176 (36), 159 (75), 143 (36), 131 (50), 129 (68), 128 (40); calcd for $C_{13}H_{14}O_2$ m/e 202.0994, measured m/e 202.1000.

The reaction of 0.251 g (1.00 mmol) of complex **1c** and 0.263 g (2.26 mmol) of 1-phenyl-1-propyne in 23 mL of hexane provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.018 g (<9%) of impure **9l**, 0.018 g (9%) of **5l**, and 0.033 g (16%) of *trans*-**4l**. When the reaction of **1c** and 1-phenyl-1-propyne in THF was repeated with the procedure described above except that the reaction was carried out under an atmosphere of carbon monoxide (1 atm at 25 °C), the product distribution and yields where essentially unchanged, as indicated in Scheme IV. The reaction of the triphenylphosphine complex **20**[36,46] with 1-phenyl-1-propyne in THF under an argon atmosphere lead to the exclusive formation of the cyclobutenone **9l**, but in only 20% yield.

Reaction of Chromium Complex 1c with the Methoxymethyl Ether of 3-Pentyn-1-ol. The reaction of 0.528 g (2.11 mmol) of complex **1c**[31] and 0.542 g (4.23 mmol) of the methoxymethyl ether of 3-pentyn-1-ol in 40 mL of hexane provided, in order of elution (1:1:10–1:1:4–1:1:1), 0.097 g (21%) of **5m** as a colorless oil and a 1.4:1 mixture of isomers (regiochemistry unassigned) and 0.067 g (15%) of *trans*-**4m** as a colorless oil and a 1.4:1 mixture of isomers (regiochemistry unassigned). Spectral data for *trans*-**4m**: ^{1}H NMR ($CDCl_3$) δ 1.11 (d, 3 H, J = 6.25 Hz, CH_3), 1.20 (d, 3 H, J = 7.10 Hz, CH_3), 1.58–1.70 (m, 2 H), 1.97–2.06 (m, 1 H), 2.06–2.15 (m, 2 H), 2.60 (m, 2 H), 2.92 (pent, 1 H), 3.31 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 3.60 (t, 2 H, J = 6.0 Hz, CH_2), 3.66 (t, 2 H, J = 6.64 Hz, CH_2), 3.78 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 4.57 (s, 2 H, OCH_2O), 4.58 (s, 2 H, OCH_2O), 5.16 (s, 1 H, 2-CH), 5.17 (s, 1 H, 2-CH); IR (CCl_4) 2975 s, 2940 s, 2910 s, 2883 s, 2846 m, 2823 m, 1704 s, 1694 s, 1613 w, 1459 m, 1440 m, 1378 s, 1348 s, 1306 m, 1300 m, 1183 w, 1166 s, 1152 s, 1123 m, 1102 m, 1085 m, 1042 m, 921 m, cm^{-1}; mass spectrum, m/e (% relative intensity) 183 M$^+$ − OCH_3 (9), 169 (34), 153 (24), 139 (10), 126 (100), 111 (28), 97 (5), 93 (5), 77 (7), 69 (14). The stereochemistry was assigned as trans on the basis that the major diastereomer of **4j** was trans. Spectral data for **5m**: ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 6 H, CH_3), 2.21 (d, 1 H, J = ~18 Hz, 5-C(H)H), 2.35 (m, 1 H), 2.47 (t, 2 H, J = 6.8 Hz, CH_2), 2.50–2.55 (m, 1 H), 2.55–2.64 (m, 1 H), 2.67–2.74 (m, 2 H), 3.27 (s, 3 H, OCH_3), 3.30 (s, 3 H, OCH_3), 3.35 (s, 6 H, OCH_3 + OCH_3), 3.53 (td, 2 H, J = 6.79, 1.49 Hz, CH_2), 3.70 (t, 2 H, CH_2), 4.29 (m, 1 H, 4-CH), 4.42 (m, 1 H, 4-CH), 4.52 (s, 2 H, OCH_2O), 4.57 (s, 2 H, OCH_2O); IR (CCl_4) 2989 m, 2948 s, 2930 s, 2883 s, 2844 s, 2823 s, 1761 m, 1716 s, 1712 s, 1658 s, 1463 m, 1441 m, 1404 m, 1385 s, 1345 s, 1302 m, 1152 s, 1121 m, 1095 m, 1043 s, 921 cm^{-1}; mass spectrum, m/e (% relative intensity) 214 M$^+$ (5), 182 (16), 169 (95), 153 (35), 137 (54), 123 (25), 109 (100), 93 (21), 79 (35), 75 (11), 67 (22).

Preparation of Pentacarbonyl(n-butylmethoxycarbene)chromium(0) (1e).[34] To a solution of 5.494 g (25 mmol) of chromium hexacarbonyl in 300 mL of THF at 0 °C was added dropwise 10.4 mL (16.7 mmol) of a 1.6 M solution of nBuLi in hexanes. The resultant solution was stirred a further 40 min at 0 °C, and then the solvent was removed on a rotary evaporator. The crude oil was placed on the vacuum line for 20 min and then dissolved in H_2O and filtered through Celite. Approximately 50 mL of CH_2Cl_2 was added and the mixture placed in a warm water bath. Me_3OBF_4 was added until no further solid could be seen forming and the solution stirred 5 min. The reaction was quenched with 2 × 50 mL of aqueous $NaHCO_3$ and washed with 2 × 30 mL each of H_2O and brine and then dried over $MgSO_4$ and concentrated. The crude product was purified on SiO_2 with hexanes as eluent to give 4.248 g (14.5 mmol, 87%) of complex **1e** as a bright-orange oil. Spectral data for **1e**: ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, J = 7.2 Hz, CH_3), 1.33 (sextet, 2 H, J = 7.5 Hz, CH_2CH_3), 1.47 (pentet, 2 H, J = 7.4 Hz, CH_2Et), 3.29 (t, 2 H, J = 7.6 Hz, CH_2Pr), 4.75 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 13.76 (q, J = 124.5 Hz, Bu-CH_3), 22.40 (t, J = 126.7 Hz, CH_2), 28.37 (t, J = 130,8 Hz, CH_2), 62.85 (t, J = 124.1 Hz, CH_2Pr), 67.55 (q, J = 148.3 Hz, OCH_3), 216.45 (s, cis CO), 223.24 (s, trans CO), 363.74 (s, carbene carbon); IR (CCl_4) 2964 m, 2869 w, 2062 m, 1976 s, 1930 s, 1452 m, 1287 w, 1164 w, 1120 w, 1033 w, 906 w, 656 m cm^{-1}; calcd for $C_{11}H_{12}CrO_6$ m/e 292.0039, measured m/e 292.0042.

Reaction of Chromium Complex 1e with 1-Pentyne. The reaction of 0.427 g (1.46 mmol) of complex **1e** and 0.199 g (2.92 mmol) of 1-pentyne in 29 mL of hexane provided, in order of elution (1:1:10–1:1:4–1:1:1), phenols **10n** and **16n** as impure mixtures (which were subsequently purified and characterized) in ~5% yield each, 0.035 g of a mixture of **8n** (3%) and **5n** (2%), and 0.068 g (23%) of **4n** as a colorless oil. The yields of **8n** and **5n** were determined on the crude reaction mixture by ^{1}H NMR with Ph_3CH as internal standard. Spectral data for **4n**: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, J = 7.4 Hz, Pr-CH_3), 0.94 (t, 3 H, J = 7.1 Hz, Pr-CH_3), 1.25–1.47 (m, 5 H, 2-$CH_2$$CH_3$ + 5-C(H)C(H)HCH_2), 1.80–1.88 (m, 1 H, 5-C(H)C(H)H), 2.08 (t, 2 H, J = 7.4 Hz, 2-$CH_2$$CH_2$), 2.28 (d, 1 H, J = 17.3 Hz, 4-CH_{trans}), 2.40–2.48 (m, 1 H, 5-C(H)CH_2), 2.79 (dd, 1 H, J = 17.4, 6.9 Hz, 4-CH_{cis}), 3.91 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 13.89 (q, J = 124.6 Hz, both Pr-CH_3), 20.30 (t, J = 125.7 Hz, CH_2), 21.08 (t, J = 127.3 Hz, CH_2), 23.04 (t, J = 128.0 Hz, CH_2), 30.94 (t, J = 131.2 Hz, C-4), 33.73 (t, J = 125.9 Hz, 2-CH_2CH_2), 44.53 (d, J = 130.2 Hz, C-5), 56.14 (q, J = 146.2 Hz, OCH_3), 119.78 (s, C-2), 183.32 (s, C-3), 207.15 (s, C-1); IR (neat) 2959 s, 2931 s, 2871 s, 1689 s, 1638 s, 1463 s, 1372 s, 1342 s, 1249 s, 1168 m, 1132 m, 1078 m, 1037 m, cm^{-1}; mass spectrum, m/e (% relative intensity) 196 M$^+$ (8), 154 (100), 125 (25), 79 (8). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.46; H, 10.24. Spectral data for **5n**: ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3 H, Pr-CH_3), 0.95 (t, 3 H, Pr-CH_3), 1.40–1.57 (m, 5 H, 2-$CH_2CH_2CH_3$ + 5-CH(H)CH_2), 1.72–1.80 (m, 1 H, 5-CH(H)CH_2), 2.16 (t, 2 H, J = 7.53 Hz, 5-CH_2CH_2), 2.26–2.34 (m, 1 H, 5-C(H)Pr), 3.43 (s, 3 H, OCH_3), 4.14 (s, 1 H, 4-CH), 7.15 (s, 1 H, 3-CH); IR (neat) 2960 s, 2932 s, 2873 s, 1774 m, 1710 s, 1633 m, 1466 s, 1380 m, 1352 m, 1229 m, 1185 m, 1097 s, 959 m, 917 s, 734 s, 648 m, cm^{-1}; mass spectrum, m/e (% relative intensity) 196 M$^+$ (38), 181 (5), 167 (41), 154 (100), 139 (71), 125 (38), 107 (27), 97 (30), 91 (16), 79 (32), 67 (17). Spectral data for **8n** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3 H, J = 7.3 Hz, Pr or Bu-CH_3), 0.87 (t, 3 H, J = 7.1 Hz, Pr or Bu-CH_3), 1.00 (t, 3 H, J = 7.3 Hz, Pr or Bu-CH_3), 1.04–1.08 (m, 2 H, CH_2), 1.29 (m, 2 H, CH_2), 1.36 (m, 2 H, CH_2), 1.62–1.72 (m, 4 H, CH_2 + CH_2), 2.06 (td, 2 H, J = 8.2, 2.9 Hz, CH_2), 2.44 (t, 2 H, J = 7.7 Hz, CH_2), 3.23 (s, 3 H, OCH_3), 4.41 (s, 1 H, 6-CH), 6.82 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 13.77 (q, J = 124.9 Hz, 2 CH_3 groups), 14.29 (q, J = 124.8 Hz, CH_3), 17.73 (t, J = 129.0 Hz, CH_2), 20.36 (t, J = 129.2 Hz, CH_2), 22.05 (t, J = 126.1 Hz, CH_2), 27.42 (t, J = 130.8 Hz, CH_2), 28.73 (t, J = 129.4 Hz, CH_2), 29.35 (t, J = 126.5 Hz, C-9), 37.30 (t, J = 129.4 Hz, C-8), 54.24 (q, J = 143.9 Hz, OCH_3), 54.40 (s, C-5), 106.49 (d, J = 163.1 Hz, C-3), 141.66 (d, J = 170.5 Hz, C-6), 156.65 (s, C-2 or C-7), 163.70 (s, C-2 or C-7), 206.46 (s, C-1 or C-4), 207.18 (s, C-1 or C-4); IR (neat) 2960 s, 2935 s, 2874 s, 1744 m, 1706 s, 1669 m, 1616 m, 1464 m, 1334 m, 1209 s, 1083 m cm^{-1}; mass spectrum, m/e (% relative intensity) 292 M$^+$ (100), 257 (22), 249 (18), 231 (46), 222 (14), 203 (28), 189 (43), 175 (9), 154 (17), 135 (6), 125 (10), 105 (10), 91 (18), 85 (12), 79 (14), 72 (28), 67 (17). Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.64; H, 9.78. Spectral data for **10n**: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 7.40 Hz, CH_3), 0.96 (t, 3 H, J = 7.44 Hz, CH_3), 0.99 (t, 3 H, J = 7.37 Hz, CH_3), 1.37–1.46 (m, 2 H, Et$CH_2$$CH_3$), 1.53–1.71 (m, 6 H, CH_2), 2.47 (t, 2 H, J = 7.83 Hz, CH_2Pr), 2.52–2.63 (m, 4 H, CH_2Et), 4.48 (s, 1 H, OH), 6.76 (s, 2 H, 3+5-CH); ^{13}C NMR ($CDCl_3$) δ 14.35, 14.44, 14.59, 23.18, 23.47, 25.37, 30.42, 32.52, 32.78, 37.84, 127.89, 128.04, 134.69, 149.73; IR (CCl_4) 3621 m, 3008 w, 2959 s, 2932 s, 2873 s, 2863 s, 1477 m, 1466 m, 1456 m, 1379 m, 1350 w, 1339 w, 1322 w, 1294 w, 1289 w, 1187 m, 1150 m, 1121 m, 1091 w, 908 w cm^{-1}; mass spectrum, m/e (% relative intensity) 234 M$^+$ (30), 205 (100), 191 (20), 105 (5), 91 (9); calcd for $C_{16}H_{26}O$ m/e 234.1984, measured m/e 234.1980. Spectral data for **16n**: ^{1}H NMR ($CDCl_3$) δ 0.94–1.00 (m, 9 H, 3 CH_3 groups); 1.39 (sex, 2 H, J = 7.5 Hz, CH_2), 1.48–1.55 (m, 2 H, CH_2), 1.55–1.68 (m, 4 H, CH_2 + CH_2), 2.48–2.56 (m, 6 H, 2+4+6-CH_2), 4.49 (s, 1 H, OH), 6.55 (s, 1 H, 3-CH or 5-CH), 6.85 (s, 1 H, 3-CH or 5-CH); ^{13}C NMR ($CDCl_3$) δ 14.03 (q, J = 124.0 Hz, CH_3), 14.10 (q, CH_3), 14.23 (q, J = 123.8 Hz, CH_3), 22.78 (t, J = 124.3 Hz, CH_2), 23.10 (t, J = 125.2 Hz, CH_2), 24.21 (t, J = 126.3 Hz, CH_2), 31.66 (t, J = 125.4 Hz, CH_2), 31.80 (t, 2-CH_2, 4-CH_2, or 6-CH_2), 33.83 (t, J = 128.9 Hz, 2-CH_2, 4-CH_2, or 6-CH_2), 34.38 (t, J = 124.3 Hz, 2-CH_2, 4-CH_2, or 6-CH_2), 115.72 (d, J = 152.5 Hz, C-3 or C-5), 125.45 (s, C-2, C-4, or C-6) 130.88 (d, J = 152.0 Hz, C-3 or C-5), 132.59 (s, C-2, C-4, or C-6), 139.01 (s, C-2, C-4, or C-6), 151.25 (s, C-1); IR (neat) 3670–3340 s, 2958 s, 2930 s, 2871 s, 1509 m, 1465 s, 1417 s, 1378 m, 1267 m, 1191 m, 1165 m, 1103 s, 909 m, 735 s, cm^{-1}; mass spectrum, m/e (% relative intensity) 234 M$^+$ (33), 205 (25), 191 (100), 163 (47), 147 (23), 121 (25), 105 (13), 91 (23), 77 (15). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.80; H, 11.27.

When the reaction in hexane was either repeated in the presence of 2 equiv of triphenylphosphine or performed under a carbon monoxide atmosphere (1 atm at 25 °C) instead of argon, the product distributions were essentially unchanged, as indicated in Table I.

Reaction under 100 psi of carbon monoxide: A solution of 0.511 g (1.75 mmol) of complex **1e** and 0.239 g (3.50 mmol) of 1-pentyne in 35 mL of hexane was deoxygenated by the freeze–thaw method and placed in a Paar pressure reactor. Carbon monoxide gas was injected until the gauge indicated a pressure of 100 psi had been attained. The reaction was stirred at 70 °C for 19.5 h, at which time the solution was cooled to room temperature and the pressure released. The volatiles were removed on a rotary evaportor, and the residue was chromatographed on silica gel (1:1:10) to give one major product, 0.0068 g (18%) of **17′n** as a colorless oil. Spectral data for **17′n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, 3 H, J = 5.69 Hz, CH_3), 0.94 (t, 3 H, J = 7.32 Hz, CH_3), 1.30 (brs, 4 H, CH_2 + CH_2), 1.58 (sex, 2 H, J = 7.37 Hz, CH_2), 1.78–1.81 (m, 2 H, CH_2), 2.27 (t, 2 H, J = 7.50 Hz, CH_2), 3.15 (s, 3 H, OCH_3), 6.64 (s, 1 H, 4-CH); ^{13}C NMR ($CDCl_3$) δ 14.07 (q, J = 125.4 Hz, CH_3), 14.27 (q, J = 124.3 Hz, CH_3), 21.18 (t, J = 123.4 Hz, CH_2), 23.07 (t, J = 128.3 Hz, CH_2), 25.92 (t, J = 126.6 Hz, CH_2), 27.52 (t, J = 124.3 Hz, CH_2), 37.44 (t, J = 127.7 Hz, CH_2), 51.28 (q, J = 143. 4 Hz, OCH_3), 109.71 (s, C-5), 138.62 (s, C-3), 145.58 (d, J = 174.6 Hz, C-4), 171.56 (s, C-2); IR (neat) 2960 s, 2935 s, 2874 s, 2837 w, 1774–1758 s, 1660 w, 1465 s, 1442 m, 1381 m, 1319 s, 1271 s, 1227 m, 1212 m, 1172 s, 1148 s, 1124 s, 1107 s, 1076 s, 1070 s, 1036 w, 1017 m, 966 s, 921 w, 904 s, 881 m, 865 m, 791 w, 766 w, 748 w, 631 w cm^{-1}; mass spectrum, m/e (% relative intensity) 213 M$^+$ + 1 (3), 197 (2), 181 (18), 170 (2), 155 (100), 151 (2), 139 (7), 125 (22), 111 (3), 107 (2), 95 (10), 91 (3), 85 (8), 79 (4), 74 (3), 71 (7), 67 (12).

Reaction of Chromium Complex 1e with 3-Methyl-1-butyne. The reaction of 0.219 g (0.75 mmol) of complex **1e** and 0.102 g (1.50 mmol) of 3-methyl-1-butyne in 15 mL of hexane provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.007 g of a mixture of **8o** (2%) and **5o** (1%) and 0.028 g (19%) of **4o** as a colorless oil. The yields of **8o** and **5o** were determined on the crude reaction mixture by ^{1}H NMR through comparison with the peak heights of **4o**. Spectral data for **4o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (d, 3 H, J = 6.8 Hz, iPr-CH_3), 0.84 (t, 3 H, J = 7.3 Hz, Pr-CH_3), 0.97 (d, 3 H, J = 6.97 Hz, iPr-CH_3), 1.39 (sex, 2 H, J = 7.4 Hz, CH_2CH_3), 2.02–2.10 (m, 2 H, CH_2CH_2), 2.24–2.32 (m, 1 H, iPr-CH), 2.33 (d, 1 H, J = 17.1 Hz, 4-CH_{trans}), 2.51–2.56 (m, 1 H, 5-CH), 2.59 (dd, 1 H, J = 17.5, 7.5 Hz, 4-CH_{cis}), 3.91 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 13.92 (q, J = 124.7 Hz, Pr-CH_3), 16.37 (q, J = 119.4 Hz, iPr-CH_3), 20.72 (d, J = 129.1 Hz, iPr-CH), 21.16 (t, J = 127.4 Hz, CH_2CH_3), 23.01 (t, J = 123.0 Hz, CH_2CH_2), 26.23 (t, J = 132.8 Hz, C-4), 28.19 (q, J = 126.4 Hz, iPr-CH_3), 50.24 (d, J = 132.0 Hz, C-5), 56.26 (q, J = 145.5 Hz, OCH_3), 120.99 (s, C-2), 183.96 (s,

(34) Yamashita, A. (Upjohn). Eur. Pat. Appl. EP 146,348,

C-3), 206.81 (s, C-1); IR (neat) 2986–2910 br s, 2868 s, 1686 s, 1642–1617 s, 1465 s, 1340 s, 1255 s, 1168 s, 1123 s, 1080 s, 1036 s, 967 s, 943 s, 920 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 196 M$^+$ (20), 181 (15), 167 (5), 154 (100), 139 (5), 125 (24), 118 (1), 111 (3), 105 (2), 95 (3), 91 (4), 83 (39), 79 (5), 67 (4). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 72.96; H, 10.15. Spectral data for **5o**: ^{1}H NMR (from mixture of **8o** and **5o**, $CDCl_3$) δ 0.80–1.50 (multiplets, 13 H, iPr-CH_3 + nPr protons), 2.28–2.32 (m, 1 H, 5-CH), 2.60–2.66 (pent, 1 H, iPr-CH), 3.44 (s, 3 H, OCH_3), 4.21 (br s, 1 H, 4-CH), 7.11 (br s, 1 H, 3-CH); water CI GC mass spectrum, *m/e* (% relative intensity) 197 M$^+$ + 1 (21), 165 (100), 137 (45), 107 (1), 95 (20), 81 (1), 72 (45), 57 (1). Spectral data for **8o** (1 diastereomer, not assigned): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87–0.93 (m, 9 H, Bu-CH_3 + iPr-CH_3), 0.95 (d, 6 H, *J* = 6.87 Hz, iPr-CH_3), 1.28–1.34 (m, 2 H, CH_2), 1.34–1.52 (m, 2 H, CH_2), 2.03–2.12 (m, 3 H, CH_2Pr + iPr-CH), 2.91 (pent, 1 H, *J* = 6.79 Hz, iPr-CH), 3.22 (s, 3 H, OCH_3), 4.51 (s, 1 H, 6-CH), 6.77 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 13.84, 17.78, 17.87, 20.66, 21.01, 22.10, 25.34, 28.85, 29.53, 54.22 (q, OCH_3), 57.73 (s, C-5), 105.83 (d, C-6), 140.16 (d, C-3), 157.06 (s, C-2), 169.47 (s, C-7), 206.57 (s, C-1 + C-4); IR (CCl_4) 2965 w, 2935 w, 2874 w, 1741 w, 1699 vs, 1671 w, 1466 w, 1390 w, 1372 w, 1347 w, 1146 w, 1125 w, 1080 w, 909 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 292 M$^+$ (48), 249 (100), 217 (35), 190 (9), 175 (32), 151 (9), 91 (10), 72 (28), 57 (16); calcd for $C_{18}H_{28}O_3$ *m/e* 292.2038, measured *m/e* 292.2034.

Reaction of Chromium Complex 1e with 3,3-Dimethyl-1-butyne. The reaction of 0.202 g (0.69 mmol) of complex **1e** and 0.283 g (3.45 mmol) of 3,3-dimethyl-1-butyne in 14 mL of hexane provided, in order of elution (1:1:10–1:1:4–Et_2O), 0.014 g of a mixture of **8p** (8%) and **5p** (3%) and 0.047 g (33%) of **4p** as a white solid. The yields of **8p** and **5p** were determined by ^{1}H NMR through comparison of relative peak heights. In a couple of reactions, a slightly impure compound tentatively assigned as furan **13p** was isolated. Spectral data for **4p**: mp = 52 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3 H, *J* = 7.0 Hz, Pr-CH_3), 0.98 (s, 9 H, tBu-CH_3), 1.37 (sex, 2 H, *J* = 7.5 Hz, CH_2CH_3), 2.04 (octet, 2 H, *J* = 7.5 Hz, CH_2CH_2), 2.23 (dd, 1 H, *J* = 6.99, 2.53 Hz, 5-CH), 2.37 (d, 1 H, *J* = 17.6 Hz, 4-CH_{trans}), 2.63 (dd, 1 H, *J* = 17.5, 6.9 Hz, 4-CH_{cis}), 3.90 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 13.84 (q, *J* = 125.3 Hz, Pr-CH_3), 21.11 (t, *J* = 127.1 Hz, CH_2), 23.00 (t, *J* = 127.4 Hz, CH_2), 27.31 (q, *J* = 126.3 Hz, tBu-CH_3), 27.94 (t, C-4), 32.94 (s, *C*-$(CH_3)_3$), 53.83 (d, *J* = 129.5 Hz, C-5), 56.06 (q, *J* = 145.7 Hz, OCH_3), 120.97 (s, C-2), 182.59 (s, C-3), 205.87 (s, C-1); IR (neat) 2959 s, 2932 s, 2871 s, 1684 s, 1625 s, 1464 s, 1364 s, 1341 s, 1252 s, 1169 m, 1132 m, 1079 m, 920 m, 734 s cm^{-1}; mass spectrum, *m/e* (% relative intensity) 210 M$^+$ (10), 195 (10), 181 (2), 154 (100), 139 (4), 125 (27), 111 (3), 95 (3), 91 (2), 83 (34), 77 (3), 67 (2); calcd for $C_{13}H_{22}O_2$ *m/e* 210.1620, measured *m/e* 210.1617. Spectral data for **5p**: ^{1}H NMR (from a mixture of **5p** and **8p**, $CDCl_3$) δ 0.94 (t, 3 H, Pr-CH_3), 1.18 (s, 9 H, tBu-CH_3), 1.71–1.78 (m, 1 H, 5-C(H)C(H)*H*), 2.25–2.29 (m, 1 H, 5-CH), 3.43 (s, 3 H, OCH_3), 4.05 (s, 1 H, 4-CH), 7.15 (d, 1 H, *J* = 2.2 Hz, 3-CH), 3 protons not assigned; ^{13}C NMR ($CDCl_3$) δ 14.17 (q, Pr-CH_3), 20.32 (t, CH_2), 28.13 (q, tBu-CH_3), 31.72 (t, CH_2), 31.84 (s, *C*$(CH_3)_3$), 53.34 (d or q, C-5 or CH_2), 56.84 (d or q, C-5 or CH_2), 82.28 (d, C-4), 149.57 (d, C-3), 155.31 (s, C-2), 206.88 (s, C-1); GC mass spectrum (CI, H_2O), *m/e* (% relative intensity) 210 M$^+$ (2), 179 (100), 161 (2), 150 (9), 126 (3), 106 (3), 73 (42), 57 (2). Spectral data for **8p** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3 H, *J* = 7.2 Hz, Bu-CH_3), 0.96 (s, 9 H, tBu-CH_3), 1.30 (s, 9 H, tBu-CH_3), 1.28–1.36 (m, 2 H, CH_2), 1.36–1.43 (m, 2 H, CH_2), 2.09 (m, 2 H, CH_2Pr), 3.20 (s, 3 H, OCH_3), 4.65 (s, 1 H, 6-CH), 6.74 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 13.86 (q, *J* = 126.0 Hz, Bu-CH_3), 22.08 (t, *J* = 124.7 Hz, CH_2), 26.44 (q, *J* = 125.1 Hz, tBu-CH_3), 28.15 (q, *J* = 126.5 Hz, tBu-CH_3), 28.88 (t, CH_2), 29.57 (t, *J* = 126.4 Hz, CH_2), 33.31 (s, *C*$(CH_3)_3$), 35.78 (s, *C*$(CH_3)_3$), 54.09 (q, *J* = 143.4 Hz, OCH_3), 60.41 (s, C-5), 104.11 (d, *J* = 163.1 Hz, C-6), 140.57 (d, *J* = 169.7 Hz, C-3), 156.95 (s, C-2), 170.38 (s, C-7), 206.53 (s, C-1 or C-4), 206.68 (s, C-1 or C-4); IR (CCl_4) 2985 w, 2963 m, 2936 m, 2907 w, 2873 w, 2840 w, 1739 w, 1696 vs, 1669 w, 1458 w, 1401 w, 1371 w, 1364 w, 1308 w, 1156 w, 1082 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 320 M$^+$ (6), 264 (100), 249 (33), 231 (5), 217 (19), 207 (7), 189 (8), 175 (6), 165 (5), 151 (4), 137 (3), 121 (3), 111 (4), 99 (6), 91 (5), 79 (4), 67 (8). Spectral data for **13p**: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3 H, nBu-CH_3), 1.22 (s, 9 H, tBu-CH_3), 1.34–1.42 (m, 2 H, CH_2CH_3), 1.53–1.61 (m, 2 H, $CH_2CH_2CH_3$), 2.48 (t, 2 H, 5-CH_2CH_2), 3.82 (s, 3 H, OCH_3), 5.73 (s, 1 H, 4-CH); IR (CCl_4) 2963 s, 2906 s, 2871 s, 1712 m, 1699 m, 1640 s, 1587 s, 1479 m, 1462 s, 1373 m, 1363 m, 1250 m, 1220 m, 1206 m, 1130 m, 1091 m, 1068 m, 991 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 210 M$^+$ (53), 195 (100), 179 (32), 167 (82), 149 (5), 137 (18), 121 (6), 107 (16), 93 (15), 85 (15), 77 (10), 67 (11).

Reaction of Chromium Complex 1e with Diphenylacetylene. The reaction of 0.268 g (0.91 mmol) of complex **1e** and 0.180 g (1.01 mmol) of diphenylacetylene in 18 mL of hexane provided (after oxidation for 12 h with 3.50 g, 7 equiv, of $[Fe(DMF)_3Cl_2][FeCl_4]$ complex[33]), in order of elution (1:1:30–1:1:10–1:1:4–1:1:1), 0.024 g (8%) of **14q**, 0.025 g (9%) of **5q**, 0.074 g (26%) of *trans*-**4q**, and 0.013 g (3%) of *cis*-**4q**, all as viscous colorless oils. Spectral data for *trans*-**4q**: ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, *J* = 7.36 Hz, Pr-CH_3), 1.61 (pent, 2 H, *J* = 7.5 Hz, CH_2CH_3), 2.34 (t, 2 H, *J* = 7.86 Hz, CH_2CH_2), 3.44 (d, 1 H, *J* = 1.91 Hz, 4-CH), 3.69 (s, 3 H, OCH_3), 4.05 (s, 1 H, 5-CH), 7.09 (d, 1 H, *J* = 7.21 Hz, aryl 2-CH or 6-CH), 7.16 (d, 1 H, *J* = 7.18 Hz, aryl 2-CH or 6-CH), 7.22–7.48 (m, 8 H, aryl CH); ^{13}C NMR ($CDCl_3$) δ 14.12 (q, *J* = 124.6 Hz, Pr-CH_3), 21.64 (t, *J* = 126.3 Hz, CH_2CH_3), 23.68 (t, *J* = 127.0 Hz, CH_2CH_2), 53.95 (d, J = 133.8 Hz, C-4 or C-5), 57.34 (q, *J* = 146.5 Hz, OCH_3), 62.73 (d, *J* = 132.5 Hz, C-4 or C-5), 122.58 (s, 4-aryl C-1), 126.78 (d, *J* = 158.6 Hz, aryl C), 127.11 (d, aryl C), 127.55 (d, *J* = 157.1 Hz, aryl C), 128.91 (d, *J* = 157.8 Hz, aryl C), 129.48 (d, *J* = 161.1 Hz, aryl C), 139.79 (s, C-2 or 5-aryl C-1), 140.31 (s, C-2 or 5-aryl C-1), 183.36 (s, C-3), 203.56 (s, C-1); IR (neat) 3062 s, 3028 s, 2958 s, 2927 s, 2870, 1686 s, 1628 s, 1496 s, 1460 s, 1340 s, 1255 s, 1167 s, 1126 s, 1081 s, 1034 s, 1002 m, 943 s, 911 s, 761 s, 728 s, 696 s, 646 s, 567 m cm^{-1}; mass spectrum, *m/e* (% relative intensity) 306 M$^+$ (100), 291 (16), 278 (29), 263 (6), 245 (13), 229 (11), 215 (46), 202 (10), 187 (34), 178 (17), 167 (9), 153 (7), 141 (6), 117 (63), 105 (15), 91 (77), 82 (14), 77 (13); calcd for $C_{21}H_{22}O_2$ *m/e* 306.1620, measured *m/e* 306.1626. The stereochemistry of the major isomer was assigned as trans on the basis that the major diastereomer of **4j** was trans. Spectral data for *cis*-**4q**: ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 3 H, *J* = 7.35 Hz, Pr-CH_3), 1.63 (sex, 2 H, *J* = 7.43 Hz, CH_2CH_3), 2.35 (td, 2 H, *J* = 7.18, 3.51 Hz, CH_2Et), 3.70 (s, 3 H, OCH_3), 4.11 (d, 1 H, *J* = 7.44 Hz, 4-CH), 4.54 (d, 1 H, *J* = 7.41 Hz, 5-CH), 6.71 (d, 2 H, *J* = 6.76 Hz, aryl 2+6-CH), 6.81 (d, 2 H, *J* = 6.99 Hz, aryl 2+6-CH), 6.90–6.96 (m, 3 H, aryl CH), 6.96–7.04 (m, 3 H, aryl CH); ^{13}C NMR ($CDCl_3$) δ 14.26 (q, CH_3), 21.64 (t, CH_2), 23.56 (t, CH_2), 49.69 (d), 56.90 (d or q), 57.86 (d or q), 123.14 (s, C-2), 126.22 (d, aryl C-4), 126.97 (d, aryl C-4), 127.58 (d, aryl CH), 128.27 (d, aryl CH), 128.56 (d, aryl CH), 130.21 (d, aryl CH), 136.25 (s, aryl C-1), 136.70 (s, aryl C-1), 182.33 (s, C-3), 204.10 (s, C-1); IR (CCl_4) 3029 w, 2962 m, 2931 m, 2872 w, 2858 w, 1700 s, 1638 s, 1454 m, 1379 w, 1362 m, 1311 m, 1161 w, 1123 m, 1036 w, 944 w, 908 w, 696 w cm^{-1}; mass spectrum *m/e* (% relative intensity) 306 M$^+$ (69), 278 (19), 245 (12), 215 (43), 187 (30), 125 (16), 105 (16), 91 (100), 77 (11); calcd for $C_{21}H_{22}O_2$ *m/e* 306.1620, measured *m/e* 306.1623. Spectral data for **5q**: ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3 H, *J* = 7.12 Hz, Pr-CH_3), 1.53–1.64 (m, 2 H, CH_2CH_3), 1.64–1.71 (m, 1 H, 5-C(H)C(H)*H*), 1.75–1.83 (m, 1 H, 5-C(H)C(*H*)H), 2.66 (br t, 1 H, *J* = 6.64 Hz, 5-C(*H*)Pr), 3.37 (s, 3 H, OCH_3), 4.72 (s, 1 H, 4-CH), 7.17–7.82 (m, 2 H, aryl CH), 7.23–7.34 (m, 6 H, aryl CH), 7.36 (d, 2 H, *J* = 7.82 Hz, aryl CH); ^{13}C NMR ($CDCl_3$) δ 14.15 (q, *J* = 124.7 Hz, Pr-CH_3), 20.46 (t, *J* = 126.5 Hz, CH_2CH_3), 32.88 (t, *J* = 127.8 Hz, CH_2CH_2), 50.96 (d, *J* = 130.4 Hz, C-2), 56.30 (q, *J* = 142.1 Hz, OCH_3), 84.23 (d, *J* = 145.5 Hz, C-3), 128.15 (d, *J* = 123.3 Hz, aryl CH), 128.30 (d, 2 aryl CH carbons), 128.78 (d, aryl CH), 129.55 (d, 2 aryl CH carbons), 131.24 (s, C-3 or aryl C-1), 133.97 (s, C-3 or aryl C-1), 140.59 (C-3 or aryl C-1), 163.65 (s, C-2), 206.02 (s, C-1); IR (neat) 3057 w, 3024 w, 2958 m, 2931 m, 2872 m, 2824 w, 1752 w, 1706 s, 1628 m, 1599 w, 1488 m, 1445 m, 1349 s, 1312 m, 1219 w, 1185 w, 1157 m, 1105 s, 1030 w, 1001 w, 958 w, 913 w, 769 m, 733 m, 696 s, 638 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 306 M$^+$ (96), 291 (14), 275 (30), 264 (100), 249 (65), 231 (25), 217 (41), 202 (25), 191 (20), 178 (56), 165 (11), 152 (14), 141 (7), 129 (12), 115 (26), 105 (20), 91 (49), 77 (16), 71 (8); calcd for $C_{21}H_{22}O_2$ *m/e* 306.1620, measured *m/e* 306.1606. Spectral data for **14q**: ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3 H, *J* = 7.33 Hz, CH_3), 1.28 (sex, 2 H, *J* = 7.52 Hz, CH_2CH_3), 1.61 (pent, 2 H, *J* = 7.49 Hz, CH_2CH_2Et), 2.55 (t, 2 H, *J* = 7.46 Hz, CH_2Pr), 3.76 (s, 3 H, OCH_3), 7.02–7.08 (m, 4 H, aryl CH), 7.17 (m, 6 H, aryl CH); ^{13}C NMR ($CDCl_3$) δ 13.84 (q, CH_3), 22.15 (t, CH_2), 25.56 (t, CH_2), 41.29 (t, CH_2Pr), 52.55 (q, OCH_3), 128.00 (d, aryl CH), 128.48 (d, aryl CH), 129.24 (d, aryl CH), 129.57 (s), 130.14 (d, aryl CH), 133.18 (s), 134.27 (s), 134.73 (s), 151.10 (s), 168.49 (s, C-1), 205.58 (s, C-4), 1 aryl carbon not located; IR (CCl_4) 3061 w, 2960 m, 2933 m, 2901 w, 2874 m, 1719 s, 1705 s, 1456 w, 1444 m, 1431 m, 1380 w, 1350 w, 1316 w, 1298 m, 1184 w, 1157 w, 1136 m, 1091 w, 1039 w, 908 w cm^{-1}; mass spectrum, *m/e* (% relative intensity) 322 M$^+$ (4), 290 (11), 265 (100), 237 (44), 194 (26), 179 (27), 105 (14), 85 (24), 57 (34); calcd for $C_{21}H_{22}O_3$ *m/e* 322.1569, measured *m/e* 322.1561.

Preparation of Pentacarbonyl(benzylmethoxycarbene)chromium Complex (1d). To a solution of 8.10 g (36.8 mmol) of chromium hexacarbonyl in 300 mL of THF at room temperature under argon was added 24 mL of a 1.4 M solution (33.5 mmol) of benzylmagnesium chloride in THF and the resulting mixture stirred at room temperature for 1 h. At this time 6.40 g (43.5 mmol) of Me_3OBF_4 was added and the solution stirred for 15 min. The reaction mixture was then quenched with aqueous $NaHCO_3$, washed with brine, dried over $MgSO_4$, and concentrated. The crude complex was purified on silica gel with hexane as eluent to give 1.54 g (14%) of the desired product as a bright-orange solid: mp = 35–36 °C (lit. mp = 39 °C[35]); ^{1}H NMR ($CDCl_3$) δ 4.65 (s, 2 H, CH_2), 4.81 (s, 3 H, OCH_3), 7.16 (d, 2 H, J = 7.2 Hz, aryl CH), 7.29 (t, 1 H, J = 7.4 Hz, aryl CH), 7.34 (t, 2 H, J = 7.6 Hz, aryl CH); ^{13}C NMR ($CDCl_3$) δ 67.76 (q, J = 148.1 Hz, OCH_3), 68.00 (t, J = 129.7 Hz, CH_2), 126.88 (d, J = 160.4 Hz, aryl C-4), 128.48 (d, J = 160.8 Hz, 2 aryl CH), 129.45 (d, J = 159.0 Hz, 2 aryl CH), 134.87 (s, aryl C-1), 216.17 (s, cis CO), 223.00 (s, trans CO), 358.32 (s, carbene carbon); IR (CCl_4) 3031 w, 2960 w, 2064 s, 1983 s, 1927–1965 s, 1454 s, 1306 w, 1147 w, 1032 w, 666 w cm^{-1}; CI mass spectrum, m/e (% relative intensity) 326 M$^+$ (3), 298 (6), 270 (24), 242 (39), 229 (5), 214 (6), 187 (52), 171 (4), 163 (5), 145 (9), 135 (7), 117 (29), 105 (96), 91 (100), 79 (33), 69 (15); calcd for $C_{14}H_{10}O_6Cr$ M$^+$ − 3CO m/e 242.0035, measured m/e 242.0026.

Reaction of the Benzyl Chromium Complex 1d with 3,3-Dimethyl-1-butyne. The reaction of 0.423 g (1.30 mmol) of complex **1d** and 0.214 g (2.60 mmol) of 2,2-dimethyl-1-butyne in 26 mL of hexane provided, in order of elution (1:1:30–1:1:10–1:1:4), 0.031 g (7%) of **8r** as a bright-yellow waxy semisolid and 0.054 g (17%) of **4r** as a white solid. *cis*- and *trans*-β-methoxystyrene and olefin isomers of the lactone **17r** were detected in the ^{1}H NMR spectra of impure fractions. When the reaction was run at 0.02 M in carbene complex at 104 °C, a 28% yield of **4r** was obtained. Spectral data for **4r**: mp = 93 °C; ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 9 H, tBu-CH_3), 2.40 (m, 1 H, 5-CH), 2.54 (dd, 1 H, J = 17.9, 2.7 Hz, 4-CH_{trans}), 2.81 (dd, 1 H, J = 17.8, 7.2 Hz, 4-CH_{cis}), 3.98 (s, 3 H, OCH_3), 7.21 (t, 1 H, J = 7.3 Hz, aryl 4-CH), 7.33 (t, 2 H, J = 7.6 Hz, aryl 3+5-CH), 7.66 (d, 2 H, J = 7.8 Hz, aryl 2+6-CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.44 (q, J = 124.7 Hz, tBu-CH_3), 28.29 (t, J = 131.8 Hz, C-4), 33.37 (d, J = 14 Hz, $C(CH_3)_3$), 54.05 (d, J = 125.8 Hz, C-5), 56.80 (q, J = 146.6 Hz, OCH_3), 119.01 (s, C-2), 126.85 (d, J = 149.6 Hz, aryl C-4), 127.89 (d, J = 159.3 Hz, 2 aryl CH), 128.33 (d, J = 158.4 Hz, 2 aryl CH), 130.84 (s, aryl C-1), 182.80 (s, C-3), 204.03 (s, C-1); IR (CCl_4) 3058 w, 2959 s, 2907 m, 2867 m, 1691 s, 1638 s, 1460 m, 1446 m, 1395 w, 1367 w, 1354 s, 1304 m, 1171 m, 1054 m, 949 w, 909 w cm^{-1}; mass spectrum, m/e (% relative intensity) 244 M$^+$ (10), 229 (9), 188 (100), 173 (26), 156 (5), 145 (7), 128 (6), 115 (6), 103 (4), 89 (8), 77 (4); calcd for $C_{16}H_{20}O_2$ m/e 244.1463, measured m/e 244.1465. Spectral data for **8r** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 9 H, tBu-CH_3), 1.30 (s, 9 H, tBu-CH_3), 3.16 (s, 3 H, OCH_3), 3.49 (d, 2 H, J = 3.6 Hz, CH_2Ph), 4.73 (s, 1 H, 6-CH), 6.75 (s, 1 H, 3-CH), 7.15–7.21 (m, 3 H, aryl CH), 7.26–7.30 (m, 2 H, aryl CH); ^{13}C NMR ($CDCl_3$) δ 26.45 (q, J = 126.5 Hz, tBu-CH_3), 28.11 (q, J = 128.3 Hz, tBu-CH_3), 33.33 (s, $C(CH_3)_3$), 35.83 (s, $C(CH_3)_3$), 36.69 (t, J = 128.0 Hz, CH_2Ph), 54.39 (q, J = 143.3 Hz, OCH_3), 60.68 (s, C-5), 106.57 (d, J = 163.6 Hz, C-6), 126.47 (d, J = 161.7 Hz, aryl C-4), 128.33 (d, J = 157.6 Hz, 2 aryl CH), 128.56 (d, J = 159.5 Hz, 2 aryl CH), 137.29 (s, aryl C-1), 140.69 (d, J = 169.4 Hz, C-3), 154.56 (s, C-2), 170.42 (s, C-7), 206.40 (s, C-1 + C-4); IR (CCl_4) 2965 m, 2938 m, 2907 w, 2870 w, 1718 w, 1696 s, 1669 w, 1454 w, 1401 w, 1372 w, 1364 w, 1152 w, 1081 w, 908 w, 884 w cm^{-1}; mass spectrum (CI), m/e (% relative intensity) 355 M$^+$ + 1 (29), 339 (5), 327 (6), 299 (40), 298 (39), 283 (4), 267 (15), 245 (5), 229 (32), 213 (71), 199 (14), 185 (100), 169 (21), 159 (21), 137 (23), 129 (24), 117 (27), 105 (34), 91 (75), 83 (51), 69 (67).

Reaction of the Benzyl Chromium Complex 1d with Pyridine. A solution of 0.209 g (0.64 mmol) of complex **1d** and 2.934 g (37.0 mmol, 3 mL) of pyridine was deoxygenated by the freeze–thaw method and stirred at 98 °C for 20 h, after which time TLC indicated no starting material remained. The excess pyridine was removed under high vacuum (0.01 mmHg) and the crude purified on silica gel (1:1:30) to give β-methoxystyrene **18** (0.038 g, 44%) as a colorless liquid as a 3.27:1 mixture of cis and trans isomers. The stereochemistry was assigned on the basis of the coupling constants of the vinyl protons in the ^{1}H NMR. Spectral data for **18**: ^{1}H NMR (mixture of isomers, $CDCl_3$) δ 3.69 (s, 3 H, OCH_3 trans), 3.78 (s, 1 H, 3 H, OCH_3 cis), 5.23 (d, 1 H, J = 7.03 Hz, 3-CH cis), 5.81 (d, J = 12.98 Hz, 3-CH trans), 6.13 (d, 1 H, J = 7.12 Hz, 2-CH cis), 7.04 (d, 1 H, J = 13.01 Hz, 2-CH trans) + aryl protons.

Preparation of Pentacarbonyl[methoxy(2-(trimethylsilyl)ethyl)carbene]chromium Complex (1f). A solution of 3.381 g (13.52 mmol) of complex **1c**[31] in 300 mL of ether was cooled to −78 °C, and 8.45 mL of a 1.6 M solution (13.52 mmol) of nBuLi in hexane was added dropwise. The anion of **1c** was assumed to have formed after 1 h and was transferred via cannula to 4.827 g (20.43 mmol) of ((trimethylsilyl)methyl) triflate (produced in 77% yield by the reaction of the commercially available (trimethylsilyl)methanol with 1 equiv of triflic anhydride and 1 equiv of pyridine in CH_2Cl_2 at 25 °C) in 300 mL ether at 25 °C. Immediately after addition, TLC (hexanes) indicated the presence of **1c** and a new nonpolar yellow compound. After the reaction mixture was stirred an additional 30 min at 25 °C, the TLC did not indicate further progress. The mixture was then quenched by adding saturated aqueous NH_4Cl. The ether layer was then extracted with brine and dried over Na_2SO_4. After filtration through Celite and removel of the volatiles, a crude yellow oil was obtained. Complex **1f** is fairly sensitive to oxidation and is air oxidized with the formation of a green precipitate under seemingly random conditions. Nonetheless, this complex was purified from the crude reaction mixture by silica gel chromatography in the presence of air with hexanes as eluent to give 0.381 g of recovered **1c** and 2.951 g (65%, 73% based on recovered starting material) of the desired product **1f** as a yellow oil. Spectral data for **1f**: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 2.13–2.20 (m, 2 H), 3.14–3.20 (m, 2 H), 4.72 (broad s, 3 H); ^{13}C NMR ($CDCl_3$) δ 1.94 (q, J = 119.0 Hz), 13.96 (t, J = 120.4 Hz), 56.70 (t, J = 129.6 Hz), 67.40 (q, J = 149.0 Hz), 216.57 (s), 223.19 (s), 363.32 (s); IR (CH_2Cl_2) 2900–3000 w, 2062 s, 1937 s, 1035 w, 859 w, 548 w cm^{-1}; mass spectrum, m/e (% relative intensity) 336 M$^+$ (11), 308 (4), 293 (1), 280 (6), 265 (2), 252 (6), 151 (8), 125 (16), 108 (13), 89 (7), 80 (28), 73 (57). Anal. Calcd for $C_{12}H_{16}O_6SiCr$: C, 42.85; H, 4.80. Found: C, 42.42; H, 4.79.

Reaction of the ((Trimethylsilyl)ethyl)chromium Complex 1f with 3,3-Dimethyl-1-butyne. The reaction of 0.270 g (0.80 mmol) of complex **1f** and 0.132 g (1.60 mmol) of 3,3-dimethyl-1-butyne in 16 mL of hexane provided, in order of elution (1:1:10), impure **8s** (yield undetermined) and 0.070 g (34%) of **4s** as a white solid. In a separate reaction, the yield of **8s** was found to be 6%. Spectral data for **4s**: mp = 48.5–49.5 °C; ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9 H, Si-CH_3), 0.99 (s, 9 H, tBu-CH_3), 1.47 (m, 2 H, CH_2Si), 2.25–2.27 (m, 1 H, 5-CH), 2.39 (d, 1 H, J = 17.6 Hz, 4-CH_{trans}), 2.65 (dd, 1 H, J = 17.5, 7.0 Hz, 4-CH_{cis}), 3.88 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 1.11 (q, J = 118.8 Hz, Si-CH_3), 10.68 (t, J = 120.8 Hz, CH_2Si), 27.51 (q, J = 125.8 Hz, tBu-CH_3), 27.86 (t, J = 153.3 Hz, C-4), 33.11 (s, $C(CH_3)_3$), 53.98 (d, J = 129.0 Hz, C-5), 55.83 (q, J = 145.0 Hz, OCH_3), 119.58 (s, C-2), 180.02 (s, C-3), 205.43 (s, C-1); IR (CCl_4) 2957 s, 2903 m, 2898 m, 2868 m, 1692 s, 1640 s, 1476 w, 1460 m, 1394 m, 1366 s, 1338 s, 1246 w, 1188 w, 1170 s, 1152 w, 1080 m, 1034 w, 908 m, 882 m, 859 m, cm^{-1}; mass spectrum, m/e (% relative intensity) 254 M$^+$ (15), 239 (100), 223 (7), 198 (56), 183 (31), 169 (12), 153 (2), 139 (1), 124 (2), 108 (3), 89 (11), 73 (77), 65 (3); calcd for $C_{14}H_{26}O_2Si$ m/e 254.1702, measured m/e 254.1712. Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.08; H, 10.30. Found: C, 66.63; H, 10.55. Spectral data for **8s** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 9 H, Si-CH_3), 0.62–0.68 (m, 2 H, CH_2Si), 0.97 (s, 9 HG, tBu-CH_3), 1.31 (s, 9 H, tBu-CH_3), 2.04–2.12 (m, 2 H, CH_2CH_2Si), 3.21 (s, 3 H, OCH_3), 4.71 (s, 1 H, 6-CH), 6.75 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ −1.79 (q, J = 118.8 Hz, Si-CH_3), 13.76 (t, J = 118.8 Hz, CH_2Si), 24.27 (t, J = 127.0 Hz, CH_2CH_2Si), 26.54 (q, J = 126.2 Hz, tBu-CH_3), 28.24 (q, J = 126.2 Hz, tBu-CH_3), 33.96 (s, $C(CH_3)_3$), 35.91 (s, $C(CH_3)_3$), 53.97 (q, J = 143.7 Hz, OCH_3), 60.45 (s, C-5), 103.05 (d, J = 163.1 Hz, C-6), 140.65 (d, J = 169.9 Hz, C-3), 159.29 (s, C-2), 170.51 (s, C-7), 206.66 (s, C-1 or C-4), 206.90 (s, C-1 or C-4); IR (neat) 2957 s, 2906 m, 2871 m, 1739 s, 1695 s, 1668 m, 1480 m, 1461 m, 1400 m, 1371 m, 1365 m, 1261 m, 1249 s, 1197 m, 1159 m, 1067 m, 883 m, 861 s, 839 s, 734 m, cm^{-1}; mass spectrum, m/e (% relative intensity) 364 M$^+$ (10), 349 (16), 308 (45), 293 (11), 277 (6), 261 (20), 233 (6), 203 (10), 189 (7), 175 (5), 161 (4), 89 (12), 73 (100), 57 (29); calcd for $C_{21}H_{36}O_3Si$ m/e 364.2433, measured m/e 364.2407.

Reaction of the (2-(Trimethylsilyl)ethyl)chromium Complex 1f with Diphenylacetylene. A mixture of 0.683 g (2.03 mmol) of complex **1f** and 0.368 g (2.07 mmol) of diphenylacetylene in 50 mL of hexane was deoxygenated by the freeze–thaw method and stirred at 45 °C for 4 days and provided, in order of elution (1:1:10–1:1:4), 0.054 g (8%) of **55** as a crystalline solid, 0.089 g (12%) of *cis*-**5t** as a colorless oil, 0.282 g (40%) of *trans*-**4t**, and 0.083 g (5%) of a compound that has been tentatively identified as (2-methoxy-1-phenyl-4-trimethylsilyl)-1-butenyl phenyl ketone **61**. Spectral data for *trans*-**4t**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.71 (d, 1 H, J = 13.4 Hz), 1.77 (d, 1 H, J = 13.4 Hz), 3.43 (d, 1 H, J = 1.95 Hz), 3.63 (s, 3 H), 4.08 (broad s, 1 H), 7.08 (d, 2 H, J = 7.2 Hz), 7.15 (d, 2 H, J = 7.2 Hz), 7.2–7.25 (m, 1 H), 7.25–7.3 (m, 3 H), 7.3–7.38 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.09 (q, J = 118.8 Hz), 11.27 (t, J = 120.2 Hz), 53.55 (d, J = 133.5 Hz), 56.85 (q, J = 146.04 Hz), 62.72 (d, J = 133.49 Hz), 120.90 (s), 126.61, 126.93, 127.43, 128.72, 129.33, 139.7 (s), 140.37 (s), 180.70 (s), 202.86 (s), 1 aryl carbon not located; IR (CH_2Cl_2) 2950–2861 w, 1690 s, 1625 s, 1602 m, 1496 w, 1330 w, 1173 w, 1081 m, 1068 m, 1036 w, 853 s cm^{-1}; mass spectrum, m/e (% relative intensity) 350 M$^+$ (71), 335 (49), 321 (1), 307 (2), 265 (100), 245 (5), 231 (3), 217 (7), 202 (5), 178 (4), 165 (2), 149 (6), 128

(35) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Mueller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.
(36) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.

(4), 115 (6), 91 (16), 73 (93). Anal. Calcd for $C_{22}H_{26}O_2Si$: C, 75.38; H, 7.48. Found: C, 75.56; H, 7.35. Spectral data for *cis*-**5t**: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 2.72–2.78 (m, 1 H), 3.29 (s, 3 H), 4.75 (d, 1 H, J = 2.02 Hz), 7.1–7.4 (m, 10 H), 2 methylene protons not located; IR (CH_2Cl_2) 2926–2659 m, 1737 m, 1706 s, 1350 m, 1031 m, 858 m cm^{-1}; mass spectrum, m/e (% relative intensity) 350 M$^+$ (34), 335 (55), 319 (23), 308 (5), 287 (4), 273 (5), 217 (12), 202 (8), 191 (5), 178 (9), 105 (7), 89 (23), 73 (100). Spectral data for **6l**: ^{1}H NMR ($CDCl_3$) δ −0.07 (s, 9 H), 0.80–0.85 (m, 2 H), 2.48–2.51 (m, 2 H), 3.74 (s, 3 H), 7.00–7.06 (m, 4 H), 7.10–7.20 (m, 6 H); mass spectrum, m/e (% relative intensity) 338 M$^+$ (36), 323 (39), 308 (14), 265 (24), 237 (11), 217 (8), 194 (7), 178 (27), 165 (5), 152 (5), 105 (8), 73 (100).

Preparation of Pentacarbonyl(isopropylmethoxycarbene)chromium(0) (1g).[37] To a solution of 0.247 g (0.988 mmol) of methyl carbene complex **1c**[31] in 15 mL of ether at −78 °C was added dropwise 0.62 mL (0.99 mmol) of a 1.6 M solution of nBuLi in hexanes. After 15 min, 0.16 g (0.99 mmol) of methyl triflate[36] was added and the reaction warmed to 0 °C and stirred for 1 h. The mixture was recooled to −78 °C, and a second equivalent of nBuLi was added followed in 15 min by a second equivalent of methyl triflate. This was warmed to 0 °C for 1 h, and a third equivalent of methyl triflate was added at 0 °C. After 1 h the reaction mixture was quenched with aqueous Na_2CO_3, and after the organic phase was washed with brine and dried over $MgSO_4$, the solvents were removed and the crude product was purified on SiO_2 with hexanes to give 0.115 g (0.415 mmol, 42%) of **1g** as a yellow solid (mp 46.5–47 °C). Spectral data for **1g**: ^{1}H NMR ($CDCl_3$) δ 0.98 (d, 6 H, J = 6.7 Hz), 4.17 (sept, 1 H, J = 6.7 Hz), 4.76 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 18.20, 60.10, 67.98, 216.40, 223.27, 367.67; IR (neat) 2070 m, 2935 w, 2873 w, 2061 m, 1980 s, 1894 m, 1451 m, 1343 m, 1257 w, 1112 m, 969 m. Anal. Calcd for $C_{10}H_{10}O_6Cr$: C, 43.17; H, 3.62. Found: C, 42.96; H, 3.80.

Reaction of the Isopropyl Chromium Complex 1g with 3,3-Dimethyl-1-butyne. The reaction of 0.681 g (2.45 mmol) of complex **1g** and 0.402 g (4.90 mmol) of 3,3-dimethyl-1-butyne in 49 mL of hexane provided, in order of elution (1:1:30–1:1:10), 0.055 g (11%) of **19u**, 0.093 g (12%) of **8u**, and 0.061 g (10%) of a fraction that was impure but consisted mainly of a compound that was tentatively assigned the structure of **9u**. Attempts at further purification of **9u** resulted in decomposition of the product. Spectral data for **19u**: ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H, tBu-CH_3), 1.04 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 2.81 (s, 1 H, 5-CH), 3.67 (s, 3 H, OCH_3), 4.66 (s, 1 H, 4-CH); ^{13}C NMR ($CDCl_3$) δ 20.90 (q, J = 127.9 Hz, CH_3), 23.00 (q, J = 128.3 Hz, CH_3), 27.91 (q, J = 126.5 Hz, tBu-CH_3), 33.95 (s, tBu-C), 49.40 (s, C-2), 55.56 (q, J = 143.0 Hz, OCH_3), 60.68 (d, J = 130.2 Hz, C-5), 90.65 (d, J = 169.4 Hz, C-4), 164.17 (s, C-3), 220.53 (s, C-1); IR (CCl_4) 2963 s, 2936 s, 2906 m, 2869 m, 2840 w, 1744 s, 1703 w, 1642 s, 1464 m, 1382 m, 1364 m, 1348 m, 1294 w, 1192 w, 1162 s, 1136 w, 1078 w, 1054 w, 894 w cm^{-1}. Spectral data for **8u** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9 H, tBu-CH_3), 1.02 (d, 3 H, J = 6.83 Hz, iPr-CH_3), 1.05 (d, 3 H, J = 6.72 Hz, iPr-CH_3), 1.30 (s, 9 H, tBu-CH_3), 2.18–2.24 (m, 1 H, iPr-CH), 3.18 (s, 3 H, OCH_3), 4.71 (s, 1 H, 7-CH), 6.74 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 20.17 (q, J = 126.4 Hz, iPr-CH_3), 20.47 (q, J = 126.1 Hz, iPr-CH_3), 26.48 (q, J = 126.9 Hz, tBu-CH_3), 27.24 (d, J = 124.6 Hz, iPr-CH), 28.20 (q, J = 126.4 Hz, tBu-CH_3), 33.30 (s, tBu-C), 33.85 (s, tBu-C), 54.23 (q, J = 143.4 Hz, OCH_3), 60.15 (s, C-5), 103.01 (d, J = 162.4 Hz, C-6), 140.64 (d, J = 169.7 Hz, C-3), 162.40 (s, C-2), 170.36 (s, C-7), 206.50 (s, C-1 + C-4); IR (CCl_4) 2966 s, 2938 s, 2907 s, 2872 s, 2839 w, 1739 m, 1696 s, 1666 s, 1609 w, 1461 m, 1400 m, 1385 m, 1371 s, 1307 m, 1191 w, 1145 m, 1125 m, 1104 m, 1079 w, 1042 w, 908 w, 889 w cm^{-1}; mass spectrum, m/e (% relative intensity) 306 M$^+$ (8), 250 (93), 235 (46), 218 (30), 203 (100), 189 (11), 175 (25), 165 (14), 147 (8), 135 (7), 119 (9), 107 (12), 91 (16), 86 (8), 79 (13), 73 (13), 67 (26); calcd for $C_{19}H_{30}O_3$ m/e 306.2195, measured m/e 306.2194. Spectral data for **9u**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (d, 3 H, J = 6.78 Hz, iPr-CH_3), 0.97 (d, 3 H, J = 6.81 Hz, iPr-CH_3), 1.19 (s, 9 H, tBu-CH_3), 2.05 (pent, 1 H, iPr-CH), 3.24 (s, 3 H, OCH_3), 7.92 (s, 1 H, 3-CH).

Reaction of the *tert*-Butyl Chromium Complex 1h with 3,3-Dimethyl-1-butyne. The reaction of 0.724 g (2.45 mmol) of complex **1h**[38] and 0.407 g (4.96 mmol) of 3,3-dimethyl-1-butyne in 35 mL of hexane provided, in order of elution (1:1:30–1:1:10), 0.007 g (1%) of **10v** as a white solid, 0.093 g of a mixture of **8v** (21%) and **17v** (8%), and 0.118 g (22%) of **9v**. Spectral data for **10v**: mp = 119.5–120 °C; ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9 H, 4-tBu-CH_3), 1.46 (s, 18 H, 2+6-tBu-CH_3), 5.02 (s, 1 H, OH), 7.19 (s, 2 H, 3+5-CH); ^{13}C NMR ($CDCl_3$) δ 29.70 (s, 4-tBu-C), 30.39 (q, 2+6-tBu-CH_3), 31.70 (q, 4-tBu-CH_3), 34.54 (s, 2+6-tBu-C), 121.87 (d, C-3 + C-5), 134.90 (s), 143.26 (s), 163.16 (s, C-1); IR (CCl_4) 3648 s, 2963 s, 2908 m, 2872 m, 1477 m, 1455 m, 1438 s, 1392 m, 1362 s, 1319 w, 1158 m, 1144 w, 1122 w, 879 cm^{-1}; mass spectrum, m/e (% relative intensity) 262 M$^+$ (34), 247 (100), 231 (77), 149 (4), 116 (7), 108 (3), 102 (5), 94 (6), 80 (9); calcd for $C_{18}H_{30}O$ m/e 262.2297, measured m/e 262.2300. Spectral data for **8v** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 9 H, tBu-CH_3), 1.13 (s, 9 H, tBu-CH_3), 1.31 (s, 9 H, tBu-CH_3), 3.27 (s, 3 H, OCH_3), 5.02 (s, 1 H, 7-CH), 6.80 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 26.49 (q, J = 126.5 Hz, tBu-CH_3), 28.24 (q, J = 130.2 Hz, tBu-CH_3), 29.61 (q, J = 128.3 Hz, tBu-CH_3), 33.37 (s, tBu-C), 36.18 (s, tBu-C), 36.56 (s, tBu-C), 59.95 (q, J = 144.0 Hz, OCH_3), 60.17 (s, C-5), 108.17 (d, J = 159.5 Hz, C-6), 141.04 (d, J = 169.1 Hz, C-3), 165.61 (s, C-2), 170.66 (s, C-7), 205.93 (s, C-1 or C-4), 206.11 (s, C-1 or C-4); IR (CCl_4) 2966 m, 2905 w, 2871 w, 1740 w, 1696 s, 1648 w, 1480 w, 1459 w, 1401 w, 1372 m, 1364 m, 1320 m, 1120 m cm^{-1}; mass spectrum, m/e (% relative intensity) 320 M$^+$ (4), 264 (100), 249 (27), 231 (16), 217 (27), 207 (33), 193 (28), 175 (25), 165 (5), 147 (7), 135 (3), 121 (12), 100 (8), 91 (8), 73 (97), 67 (13). Spectral data for **9v**: ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9 H, tBu-CH_3), 1.17 (s, 9 H, tBu-CH_3), 3.18 (s, 3 H, OCH_3), 7.91 (s, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 26.30 (q, tBu-CH_3), 27.61 (q, tBu-CH_3), 31.80 (s, tBu-C), 35.15 (s, tBu-C), 52.57 (q, OCH_3), 104.37 (s, C-4), 159.41 (d, C-3), 168.76 (s, C-2), 197.16 (s, C-1); IR (CCl_4) 2985 s, 2932 s, 2904 s, 2869 s, 2828 s, 1759 s, 1716 m, 1703 w, 1475, 1400 s, 1394 s, 1364 s, 1286 s, 1138 s, 1098 m, 1050 m, 935 w, 887 m, 860 w cm^{-1}. Spectral data for **17v**: ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H, tBu-CH_3), 1.23 (s, 9 H, tBu-CH_3), 4.46 (s, 1 H, 5-CH), 6.89 (s, 1 H, 4-CH); ^{13}C NMR (extracted from a mixture of **8v** and **17v**, $CDCl_3$) δ 25.33 (q, tBu-CH_3), 28.18 (q, tBu-CH_3), 31.56 (s, tBu-C), 34.79 (s, tBu-C), 87.29 (d, C-5), 143.65 (d, C-4), 202.89 (s, C-2), 1 carbon not located; IR (CCl_4) 1760 s cm^{-1}; mass spectrum, m/e (% relative intensity) 196 M$^+$ (1), 181 (9), 153 (3), 140 (89), 125 (100), 111 (4), 97 (5), 91 (2), 77 (4), 67 (12).

Reaction of Methyl Molybdenum and Tungsten Complexes 1b and 1a with 3,3-Dimethyl-1-butyne. The reaction of 0.554 g (1.88 mmol) of the molybdenum complex **1b**[39] and 0.309 g (3.76 mmol) of 3,3-dimethyl-1-butyne in 75 mL of hexane provided, (after hydrolysis of the crude solution with 10% aqueous HCl in 5 mL of THF at room temperature for 1.5 h) in order of elution (1:1:10), 0.032 g (6–8%) of **10c** plus another minor isomer as impurity and 0.070 g (29%) of **3c**. Spectral data for **3c**: ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 9 H, tBu-CH_3), 2.23 (s, 3 H, CH_3), 5.96 (d, 1 H, J = 16.26 Hz, 3-CH), 6.75 (d, 1 H, J = 16.21 Hz, 4-CH); IR (neat) 2963 s, 2907 s, 2869 s, 1698 s, 1676 s, 1624 s, 1477 m, 1451 m, 1426 m, 1392 m, 1362 s, 1318 m, 1297 m, 1255 s, 1200 m, 1190 m, 1024 m, 984 s, 917 s, 734 s cm^{-1}; mass spectrum, m/e (% relative intensity) 126 M$^+$ (21), 111 (100), 93 (8), 83 (63), 77 (7), 67 (16); calcd for $C_8H_{14}O$ m/e 126.1045, measured m/e 126.1036. Spectral data for **10c**: ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9 H, tBu-CH_3), 1.46 (s, 9 H, tBu-CH_3), 2.28 (s, 3 H, CH_3), 4.66 (s, 1 H, OH), 7.02 (s, 1 H, 3-CH or 5-CH), 7.19 (s, 1 H, 3-CH or 5-CH); mass spectrum, m/e (% relative intensity) 220 M$^+$ (20), 205 (100), 189 (3), 177 (2), 149 (2), 121 (3), 95 (3), 81 (9), 67 (5), 57 (35); calcd for $C_{15}H_{24}O$ m/e 220.1827, measured m/e 220.1823.

The reaction of 0.612 g (1.60 mmol) of the tungsten complex **1a**[39] and 0.263 g (3.20 mmol) of 2,2-dimethyl-1-butyne in 75 mL of hexane provided (after hydrolysis of the crude solution with 10% aqueous HCl in 5 mL of THF at room temperature for 1.5 h and chromatography on silica gel, 1:1:10) 0.030 g (15%) of **3c**.

Reaction of Thiophenoxy and Methylamino Chromium Complexes 21 and 24 with 3,3-Dimethyl-1-butyne. The reaction of 0.298 g (0.91 mmol) of thiophenoxy complex **21**[41] and 0.149 g (1.82 mmol) of 3,3-dimethyl-1-butyne in 18 mL of hexane provided, in order of elution (1:1:30–1:1:10–1:1:4), 0.007 g (3%) of **4w**, 0.009 g (4%) of **5w**, 0.003 g (8%) of **8w**, and 0.023 g (10%) of **9w**. Spectral data for **4w**: ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H, tBu-CH_3), 2.31 (m, 1 H, 5-CH), 2.59 (d, 1 H, J = 4-CH_{trans}), 2.79 (dd, 1 H, 4-CH_{cis}), 5.51 (s, 1 H, 2-CH), 7.38–7.46 (m, 3 H, aryl CH), 7.48–7.54 (m, 2 H, aryl CH); IR (CCl_4) 2977 m, 2962 m, 2936 w, 2898 w, 2868 m, 1691 s, 1475 w, 1460 w, 1442 w, 1395 w, 1382 w, 1367 m, 1350 w, 1168 m, 1149 w, 1122 m, 909 w cm^{-1}. Spectral data for **5w**: ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 9 H, tBu-CH_3), 2.44 (d, 1 H, 5-CH_{trans}), 2.86 (dd, 1 H, 5-CH_{cis}), 4.19 (m, 1 H, 4-CH), 7.10 (d, 1 H, 3-CH), 7.25 (m, 3 H, aryl CH), 7.34–7.42 (m, 2 H, aryl CH); IR (CCl_4) 3076 w, 3063 w, 2976 s, 2985 s, 2936 s, 2906 m, 2869 s, 2800 w, 1767 w, 1714 s, 1651 w, 1479 m, 1460 m, 1440 s, 1391 w, 1382 m,

(37) Fischer, E. O.; Plabst, E. *Chem. Ber.* **1974**, *107*, 3326.
(38) Hafner, A.; Hegedus, L. S.; deWeck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.
(39) These complexes have been reported[40a] and were prepared[40b] according to a modified procedure reported for chromium.[31]
(40) (a) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Senoff, C. V.; Lam, G. T.; Malkiewich, C. D. *Inorg. Synth.* **1978**, *17*, 95.
(41) Lam, C. T.; Senoff, C. S.; Ward, J. E. H. *J. Organomet. Chem.* **1974**, *70*, 273.

1364 s, 1350 m, 1318 m, 1301 w, 1278 w, 1168 m, 1152 m, 1125 s, 1079 w, 1043 w, 1026 w, 935 w, 909 w cm^{-1}. Spectral data for **8w** (1 diastereomer, not assigned): ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9 H, tBu-CH_3), 1.23 (s, 9 H, tBu-CH_3), 1.89 (s, 3 H, CH_3), 5.91 (s, 1 H, 6-CH), 6.81 (s, 1 H, 3-CH), 7.10–7.26 (m, 5 H, aryl CH); IR (CCl_4) 3076 w, 3062 w, 2966 s, 2937 m, 2907 m, 2870 m, 1771 m, 1738 w, 1696 s, 1479 m, 1467 w, 1458 w, 1440 m, 1403 m, 1392 w, 1374 s, 1365 m, 1350 w, 1323 w, 1306 w, 1190 w, 1139 w, 1120 m, 1026 w, 909 w, 892 w, 803 w, 691 cm^{-1}. Spectral data for **9w**: ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 9 H, tBu-CH_3), 1.58 (s, 3 H, CH_3), 7.20–7.30 (m, 3 H, aryl CH), 7.40 (d, 2 H, aryl CH), 7.51 (s, 1 H, 3-CH); IR (CCl_4) 3076 w, 3063 w, 2965 s, 2932 m, 2905 m, 2868 s, 1797 w, 1762 s, 1709 w, 1691 m, 1481 m, 1475 m, 1439 s, 1392 w, 1383 w, 1365 s, 1350 w, 1305 w, 1283 w, 1158 w, 1122 m, 1079 w, 1026 w, 910 m, 879 w, 692 cm^{-1}.

The reaction of 0.358 g (1.44 mmol) of a mixture of isomers of the methylamino complex **24**[42] and 0.237 g (2.88 mmol) of 2,2-dimethyl-1-butyne in 22 mL of hexane and 7 mL of benzene provided after chromatography on silica gel (1:1:4–1:1:1) 0.064 g (35%) of **3c**.

Reaction of Pentacarbonyl[((methoxyphenylmethylene)amino)-methylcarbene]chromium Complex (22) with 1-Pentyne in THF. The reaction of 0.274 g (0.78 mmol) of complex **22**[43] and 0.146 g (1.48 mmol) of 1-pentyne in 5 mL of THF after stirring for 4 days at 70 °C provided, in order of elution (1:1:4), 0.036 g (21%) of the 3-hydroxypyridine **23** and 0.035 g (18%) of the cyclopentenone **4x**. Spectral data for **4x**: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 7.2 Hz), 1.32 (m, 2 H), 1.78 (m, 1 H), 2.24 (dt, 1 H, J = 18.1, 1.4 Hz), 2.44 (m, 1 H), 2.69 (dd, 1 H, J = 18.2, 6.7 Hz), 3.94 (s, 3 H), 5.80 (s, 1 H), 7.37 (t, 2 H, J = 7.0 Hz), 7.46 (t, 1 H, J = 7.0 Hz), 7.55 (d, 1 H, J = 7.2 Hz); IR ($CDCl_3$) 2840 m, 1630 s, 1560 s, cm^{-1}; mass spectrum, m/e (% relative intensity) 257 M$^+$ (10), 228 (20), 215 (100), 200 (15), 185 (10), 105 (50), 77 (40), 59 (10); calcd for $C_{16}H_{19}NO_2$ m/e 257.1415, measured m/e 257.1419. Spectral data for **23**: ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.3 Hz), 1.69 (sextet, 2 H, J = 7.5 Hz), 2.50 (s, 3 H), 2.62 (t, 2 H, J = 7.5 Hz), 7.39 (s, 1 H), 7.39 (t, 1 H, J = 7.4 Hz), 7.47 (t, 2 H, J = 7.4 Hz), 7.61 (d, 2 H, J = 7.2 Hz), OH proton not observed; IR ($CHCl_3$) 3556 s, 1727 m, 1706 m, 1610 w, 1459 w, 1120 w cm^{-1}; mass spectrum, m/e (% relative intensity) 227 M$^+$ (80), 212 (100), 199 (60), 184 (10), 168 (10), 128 (10), 105 (35), 91 (10), 77 (30), 65 (10); calcd for $C_{15}H_{17}NO$ m/e 227.1310, measured m/e 227.1308.

Preparation of Aldehyde 45. Diisopropylamine (6.5 g, 64.24 mmol) was dissolved in 250 mL of THF and cooled to −78 °C. A solution of 1.6 M nBuLi (40 mL, 64 mmol) in hexane was added, and the solution was stirred for 15 min at −78 °C. To this LDA solution was added propionitrile (3.55 g, 64.45 mmol) slowly at −78 °C and the resulting reaction mixture stirred for 15 min at this temperature. The solution of the nitrile anion was added very slowly via syringe to a solution of the bromide **43** (12.4 g, 83.2 mmol) in 100 mL of THF at −78 °C and the resulting reaction mixture stirred for 25 min at −78 °C, 30 min at 0 °C, and finally 5 min at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with ether. After removal of the volatiles, the nitrile **44** was purified by distillation under reduced pressure and obtained as a colorless liquid (6.55 g, 53.25 mmol, 83%). Spectral data for **44**: ^{1}H NMR ($CDCl_3$) δ 1.29 (d, 3 H, J = 7.1 Hz), 1.62–1.78 (m, 2 H), 1.69 (s, 3 H), 2.11–2.22 (m, 2 H), 2.53–2.61 (m, 1 H), 4.69 (s, 1 H), 4.74 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.84, 22.10, 24.80, 31.78, 34.82, 111.18, 122.74, 143.47; IR (neat) 3077 m, 2980–2940 s, 2240 m, 1650 m, 1455 s, 1379 m, 1125 w, 892 s cm^{-1}; mass spectrum m/e (% relative intensity) 123 M$^+$ (20), 100 (15), 95 (10), 81 (37), 74 (13), 69 (100), 67 (14), 65 (5).

The nitrile **44** (7.0 g, 56.9 mmol) was dissolved in 500 mL of hexane, and the solution was cooled to −78 °C. DIBAL-H (1.0 M in hexanes, 60.28 mL, 60.28 mmol) was added dropwise under nitrogen at −78 °C. The solution was warmed to 0 °C and stirred for 4 h. The reaction was then quenched with dilute aqueous HCl, and the hexane layer was separated, washed with water, and dried over anhydrous $MgSO_4$, and the volatiles, removed in vacuo. The aldehyde **45** was purified by distillation under reduced pressure (4.5 g, 35.7 mmol, 63%). Spectral data for **45**: ^{1}H NMR ($CDCl_3$) δ 1.17 (d, 3 H, J = 7.1 Hz), 1.51–1.56 (m, 1 H), 1.78 (s, 3 H), 1.91–1.96 (m, 1 H), 2.09–2.15 (m, 2 H), 2.38–2.41 (m, 1 H), 4.74 (s, 1 H), 4.78 (s, 1 H), 9.65 (d, 1 H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.27, 22.26, 28.32, 34.89, 45.72, 110.63, 144.80, 204.93; IR (neat) 3075 m, 2970–2934 s, 2712 m, 1726 s, 1650 m, 1456 s, 1376 m, 889 s cm^{-1}.

Preparation of 1-Methoxy-3,6-dimethyl-1,6-heptadiene (47). (Methoxymethyl)trimethylsilane (5.72 g, 48.3 mmol) in 70 mL of THF was cooled to −78 °C, and a solution of 1.3 M sBuLi (37 mL, 48.3 mmol) in hexanes was slowly added via syringe.[27] The mixture was warmed to −25 °C and held at this temperature for 30 min to ensure complete carbanion formation. This pale-yellow solution was cooled to −35 °C, and the aldehyde **45** (5.3 g, 42 mmol) was added. The mixture was slowly allowed to warm to 25 °C over 1.5 h and then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The ether layer was washed with water and brine, dried over anhydrous $MgSO_4$, and stripped of volatiles in vacuo. The product alcohol **46** was purified by silica gel column chromatography (6.82 g, 27.95 mmol, 67%) and obtained as a mixture of four diastereomers as a colorless oil. Spectral data for **46** (obtained on the mixture of isomers; the NMR data are extracted and reported for the two major isomers): isomer A ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 0.941 (d, 3 H, J = 6.6 Hz), 1.27–2.19 (m, 5 H), 1.63 (s, 1 H), 1.74 (s, 3 H), 2.91–2.95 (m, 1 H), 3.32–3.39 (m, 1 H), 3.431 (s, 3 H), 4.69 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ −2.32, 14.03, 22.39, 32.26, 35.00, 35.29, 61.33, 75.55, 78.27, 109.92, 145.94; isomer B ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.942 (d, 3 H, J = 7.9 Hz), 1.27–2.19 (m, 5 H), 1.63 (br s, 1 H), 1.74 (s, 3 H), 2.91–2.95 (m, 1 H), 3.32–3.39 (m, 1 H), 3.430 (s, 3 H), 4.69 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ −1.79, 16.69, 22.51, 30.21, 34.97, 35.13, 60.12, 76.08, 77.16, 109.59, 146.37; IR (neat) 3474 m, 2964–2933 s, 2819 m, 1649 w, 1451 m, 1377 m, 1248 s, 1089 m, 977 w, 885 m, 840 s cm^{-1}; mass spectrum m/e (% relative intensity) 244 M$^+$ (1), 227 (12), 208 (11), 196 (7), 175 (8), 137 (9), 123 (20), 109 (47), 89 (38), 81 (43), 73 (100).

A solution of the alcohol **46** (6.55 g, 26.8 mmol) in 150 mL of THF under nitrogen was treated with KH (12.3 g, 0.107 mol, 35% dispersion in oil, washed with pentane and decanted). The mixture was heated at 60 °C for 3–4 h and then quenched with saturated aqueous NH_4Cl solution at 0 °C and extracted with ether. The ether layer was washed with water and brine, dried over anhydrous $MgSO_4$, and stripped of volatiles in vacuo. The enol ether **47** was purified by distillation under reduced pressure and obtained as a 1:1 ratio of E/Z-isomers in 63% yield (2.6 g, 16.88 mmol). Spectral data for **47** (the NMR data for the E- and Z-isomers were extracted from the spectrum of the mixture): (E-isomer) ^{1}H NMR ($CDCl_3$) δ 0.96 (d, 3 H, J = 6.7 Hz), 1.22–1.50 (m, 2 H), 1.67 (s, 3 H), 1.91–2.03 (m, 3 H), 3.46 (s, 3 H), 4.54 (dd, 1 H, J = 12.6, 8.8 Hz), 4.62–4.64 (broad s, 2 H), 6.22 (d, 1 H, J = 12.7 Hz); ^{13}C ($CDCl_3$) δ 22.15, 22.50, 32.53, 35.55, 35.88 ,55.76, 109.08, 109.48, 145.20, 146.23; (Z-isomer) ^{1}H NMR ($CDCl_3$) δ 0.92 (d, 3 H, J = 6.7 Hz), 1.22–1.50 (m, 2 H), 1.67 (s, 3 H), 1.91–2.03 (m, 3 H), 3.52 (s, 3 H), 4.11 (dd, 1 H, J = 9.5, 6.3 Hz), 4.62–4.65 (broad s, 2 H), 5.80 (dd, 1 H, J = 6.3, 0.9 Hz); ^{13}C NMR ($CDCl_3$) δ 21.31, 22.55, 28.79, 35.67, 35.73, 59.36, 109.24, 113.27, 146.11, 146.45; IR (neat) 3074 m, 2997–2830 s, 1653 s, 1453 s, 1374 m, 1258 m, 1210 s, 1144–1100 s, 936 s, 886 s cm^{-1}; mass spectrum m/e (% relative intensity) 154 M$^+$ (7), 122 (13), 115 (10), 109 (15), 102 (34), 98 (38), 95 (14), 85 (100), 81 (19), 69 (24); calcd for $C_{10}H_{18}O$ m/e 154.1358, measured m/e 154.1388.

Photochemical Reaction of the Methyl Chromium Complex 1c with Diene 47. A solution of 0.500 g (2 mmol) of complex **1c**[31] and 0.616 g (4 mmol) of diene **47** in 20 mL of CH_3CN was deoxygenated by the freeze–thaw method, purged with argon, and irradiated for 15 h (450 W Conrad-Hanova mercury lamp, Pyrex well) at 15–20 °C. The solvent was then removed under vacuum and the yellow residue dissolved in hexane and allowed to air oxidize overnight. Filtration of the brown suspension, solvent removal, and silica gel column chromatography gave a colorless oil identified as the desired cyclobutanone **48** (0.436 g, 91%) and a 1.16:1.0 mixture of two diastereomers. Spectral data for **48** (NMR data for isomers A and B were extracted from the spectrum of the mixture): (isomer A) ^{1}H NMR ($CDCl_3$) δ 0.91 (d, 3 H, J = 6.7 Hz), 1.21–1.41 (m, 2 H), 1.35 (s, 3 H), 1.67 (s, 3 H), 1.71–1.85 (m, 1 H), 1.94–2.10 (m, 2 H), 2.77–2.82 (m, 1 H), 3.36 (s, 3 H), 3.42 (s, 3 H), 3.802 (d, 1 H, J = 7.4 Hz), 4.63–4.65 (broad s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.88, 16.75, 22.26, 31.36, 32.39, 34.79, 52.71, 58.46, 63.34, 76.85, 92.56, 110.05, 145.49, 210.63; (isomer B) ^{1}H NMR ($CDCl_3$) δ 1.00 (d, 3 H, J = 6.7 Hz), 1.21–1.41 (m, 2 H), 1.35 (s, 3 H), 1.67 (s, 3 H), 1.71–1.85 (m, 1 H), 1.94–2.10 (m, 2 H), 2.77–2.82 (m, 1 H), 3.36 (s, 3 H), 3.42 (s, 3 H), 3.796 (d, 1 H, J = 7.4 Hz), 4.65 (broad s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.88, 17.33, 22.31, 32.18, 32.53, 34.62, 52.71, 58.52, 63.66, 77.50, 92.46, 110.05, 145.49, 210.48; IR (neat) 2965–2935 s, 2834 m, 1777 s, 1649 w, 1451 m, 1378 m, 1215 m, 1113 m, 1005 m, 887 m, cm^{-1}; mass spectrum m/e (% relative intensity) 240 M$^+$ (11), 209 (30), 191 (15), 177 (23), 166 (12), 149 (17), 133 (8), 125 (17), 115 (100), 107 (15). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06; O, 19.97. Found: C, 69.95; H, 10.03; O, 19.88.

The cyclobutanone **48** was then dissolved in a small amount of ether and applied to an Al_2O_3 column (70 g, Woelm, basic, activity grade super I) and eluted quickly with ether. After removal of the solvent on a rotary evaporator, cyclobutenone **41** was isolated (0.117 g, 61%) as a colorless oil and as a 1.16:1.00 mixture of two diastereomers. Spectral data for **41** (NMR data for the major and minor isomers were extracted from the

(42) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147.
(43) Wulff, W. D.; Dragisich, V.; Huffman, J. C.; Kaesler, R. W.; Yang, D. C. *Organometallics* **1989**, *8*, 2196.

spectrum of the mixture): major isomer ^{1}H NMR ($CDCl_3$) δ 1.12 (d, 3 H, J = 6.9 Hz), 1.46 (s, 3 H), 1.53–1.60 (m, 1 H), 1.72 (s, 3 H), 1.74–1.77 (m, 1 H), 2.02 (t, br, 2 H, J = 2.5 Hz), 2.43–2.50 (m, 1 H), 3.28 (s, 3 H), 4.67 (s, 1 H), 4.71 (s, 1 H), 8.084 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.08, 20.16, 22.73, 30.62, 32.57, 35.59, 53.24, 95.92, 110.85, 145.45, 163.81, 165.04, 197.78; minor isomer ^{1}H NMR ($CDCl_3$) δ 1.11 (d, 3 H, J = 6.4 Hz), 1.457 (s, 3 H), 1.53–1.60 (m, 1 H), 1.72 (s, 3 H), 1.74–1.77 (m, 1 H), 2.02 (t, br, 2 H, J = 2.5 Hz), 2.43–2.50 (m, 1 H), 3.28 (s, 3 H), 4.67 (s, 1 H), 4.71 (s, 1 H), 8.08 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.04, 20.24, 22.73, 30.58, 32.64, 35.64, 53.24, 95.98, 110.85, 145.45, 163.76, 164.98, 197.69; IR (neat) 2967–2828 m, br, 1760 s, 1648 w, 1456 m, 1374 w, 1287 w, 1150 m, 1066 m, 880 m cm^{-1}; mass spectrum, m/e (% relative intensity) 208 M$^+$ (50), 193 (5), 177 (6), 166 (100), 151 (20), 138 (27), 133 (16), 123 (46), 111 (46), 102 (26), 93 (34); calcd for $C_{13}H_{20}O_2$ m/e 208.1463, measured m/e 208.1456.

Thermolysis of Cyclobutenone 41. A solution of 0.050 g (0.24 mmol) of cyclobutenone **41** in 50 mL of CH_3CN was deoxygenated by the freeze–thaw method, purged with argon, and heated to 70 °C for 24 h. After removal of the solvent, the residue was subjected to hydrolysis ($Et_2O/AcOH/H_2O$; 20 mL:10 mL:2 mL). The reaction mixture was then diluted with ether, washed with H_2O, saturated aqueous $NaHCO_3$, and brine, and dried over anhydrous $MgSO_4$. After the solvent was evaporated and the residue loaded onto a silica gel column, the only major compound that was mobile on silica gel was the ketone **50**, which was obtained as a 5.4:1 mixture of isomers in a total of 26% yield (0.012 g, 0.0618 mmol). Spectral data for **50** (NMR data for each isomer were extracted from the spectrum of the mixture): mp ~ 25 °C; major isomer ^{1}H NMR ($CDCl_3$) δ 0.99 (d, 3 H, J = 6.5 Hz), 1.20 (s, 3 H), 1.3–1.4 (m, 1 H), 1.6–1.7 (m, 1 H), 1.8–1.9 (m, 3 H), 2.14 (s, 3 H), 2.59 (d, 1 H, J = 18 Hz), 2.65 (d, 1 H, J = 18.9 Hz), 2.88 (d, 1 H, J = 18.9 Hz), 3.04 (d, 1 H, J = 18 Hz); minor isomer ^{1}H NMR ($CDCl_3$) δ 0.83 (d, 3 H, J = 7.3 Hz), 1.27 (s, 3 H), 1.46–1.50 (m, 1 H), 1.76–1.86 (m, 3 H), 2.15 (s, 3 H), 2.26–2.29 (m, 1 H), 2.62 (d, 1 H, J = 17.7 Hz), 2.76 (d, 1 H, J = 18.7 Hz), 2.85 (d, 1 H, J = 18.7 Hz), 3.31 (d, 1 H, J = 17.7 Hz); major isomer ^{13}C NMR ($CDCl_3$) δ 14.27, 21.31, 29.91, 32.45, 40.34, 40.66, 43.34, 44.68, 56.65, 72.74, 206.45, 213.98; minor isomer ^{13}C NMR ($CDCl_3$) δ 16.16, 22.05, 29.76, 31.16, 39.15, 40.09, 40.73, 43.95, 57.31, 72.62, 206.32, 216.82; IR (CH_2Cl_2) 2953 m, 2932 m, 2870 m, 1768 s, 1718 s, 1457 m, 1387 m, 1364 m, 1240 w, 1172 m, 1073 m cm^{-1}; mass spectrum, m/e (% relative intensity) 194 M$^+$ (1), 179 (1), 166 (1), 152 (55), 137 (15), 123 (7), 109 (100), 95 (52), 91 (5), 81 (22), 77 (5), 67 (25). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.17; H, 9.34. Found: C, 74.30; H, 9.28. The major isomer of **50** has been assigned as that which has a trans relationship of the two methyl groups on the five-membered ring.[32]

The bicycloheptanone **49** with the intact enol ether function can be isolated if the crude reaction mixture is not treated with acid and instead is directly chromatographed on silica gel that has been pretreated with triethylamine. Spectral data for **49** (pale-yellow oil; 4.5:1 mixture of two diastereomers, NMR data for each isomer were extracted from the spectrum of the mixture): major isomer ^{1}H NMR ($CDCl_3$) δ 1.05 (d, 3 H, J = 6.8 Hz), 1.26 (s, 3 H), 1.2–1.41 (m, 1 H), 1.71–1.73 (m, 1 H), 1.79 (s, 3 H), 1.87–1.97 (m, 2 H), 2.01–2.08 (m, 1 H), 2.65 (d, 1 H, J = 18 Hz), 2.74 (d, 1 H, J = 18 Hz), 3.51 (s, 3 H), 4.21 (s, 1 H); minor isomer ^{1}H NMR ($CDCl_3$) δ 0.78 (d, 3 H, J = 7.3 Hz), 1.26 (s, 3 H), 1.28–1.41 (m, 1 H), 1.71–1.73 (m, 1 H), 1.79 (s, 3 H), 1.87–1.97 (m, 2 H), 2.01–2.08 (m, 1 H), 2.65 (d, 1 H, J = 18 Hz), 2.74 (d, 1 H, J = 18 Hz), 3.53 (s, 3 H), 4.38 (s, 1 H); major isomer ^{13}C NMR ($CDCl_3$) δ 14.66, 18.95, 22.73, 32.48, 40.32, 43.00, 47.94, 54.26, 56.31, 76.60, 94.97, 156.32, 214.38; minor isomer ^{13}C NMR ($CDCl_3$) δ 16.10, 18.09, 24.04, 31.39, 37.76, 40.75, 47.94, 54.26, 56.53, 76.60, 90.56, 156.32, 214.38; IR (neat) 2867–2952 m, br, 2361 w, 2337 w, 1767 s, 1653 m, 1459 w, 1393 w, 1219 m, 1076 w cm^{-1}; mass spectrum, m/e (% relative intensity) 208 M$^+$ (4), 193 (3), 166 (100), 151 (45), 138 (37), 133 (15), 123 (51), 119 (12), 107 (26), 95 (7), 93 (25), 91 (24), 85 (8); calcd for $C_{13}H_{20}O_2$ m/e 208.1463, measured m/e 208.1472. The major isomer was determined to have the E-olefin geometry on the basis of the following data from an NOE proton experiment: irradiation at δ 3.51 (methoxyl) resulted in an 11% enhancement at δ 4.21 (vinyl); irradiation at δ 4.21 (vinyl) produced a 2% enhancement at δ 3.51 (methoxyl). The minor isomer was also assigned as having the E-olefin geometry by correlation of the ^{13}C NMR spectra of all four isomers of **49**.[32]

Preparation of *trans*-Pentacarbonyl[methoxy(2-(trimethylsilyl)vinyl)-carbene]chromium Complex 54. A solution of 2.84 g (7.30 mmol) of tri-n-butyl-(*trans*-2-(trimethylsilyl)vinyl)stannane[44] in 60 mL of THF was cooled to −78 °C, and 4.6 mL (7.36 mmol) of a 1.6 M solution of nBuLi in hexane was added dropwise by syringe. At this time, the cold bath was removed and the solution was allowed to stir for 40 min. The anion was assumed to have formed, and the solution was transferred to a suspension of 1.787 g (8.12 mmol) of $Cr(CO)_6$ in 300 mL of THF. After the reaction mixture was stirred under argon for 1 h, the flask was opened to air and the volatiles were removed on a rotary evaporator and under high vacuum (0.01 mmHg). The residue was taken up in 200 mL of CH_2Cl_2 and cooled to 0 °C. After the addition of 1.731 g (11.70 mmol) of Me_3OBF_4 and 1 mL of H_2O, the ice/water bath was removed and the methylene chloride solution immediately diluted with 300–400 mL of hexanes. In this way, the alkylated product was extracted into the organic layer as it formed and with sufficient dilution to minimize by-product formation. After being allowed to stir at room temperature for 20 min, the organic layer was washed with saturated aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. Following filtration through Celite and removal of the volatiles, a black oil was obtained which required immediate purification on silica gel with hexanes and provided 0.967 g (40%) of **54** as a red oil (R_f = 0.49, hexane): ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 4.77 (s, 3 H), 6.17 (d, 1 H, J = 18 Hz), 7.53 (d, 1 H, J = 18 Hz); ^{13}C NMR ($CDCl_3$) δ −1.8, 66.6, 133.3, 154.1, 216.5, 224.1, 338.6; IR (neat) 2929 w, 2061 m, 1926 vs, 1452 w, 1249 w, 1048 w, 985 w, 844 w.

Reaction of the (*trans*-(Trimethylsilyl)vinyl) Chromium Complex 54 with Diphenylacetylene. The carbene complex **54** (86.9 mg, 0.260 mmol) and diphenylacetylene (70.0 mg, 0.390 mmol) were dissolved in 8 mL of THF. After deoxygenation by the freeze–thaw method, the reaction vessel was heated at 60 °C with stirring for 45 h. After the reaction mixture was cooled to room temperature, volatiles were removed by rotary evaporator. The residue was taken into ~15 mL of ether and stirred with a 0.5 M solution of cerric ammonium nitrate (5 mL, 2.5 mmol) at ambient temperature for 30 min. After separation of the two layers, the aqueous layer was extracted once with ether and then the combined organic layers were dried (brine, magnesium sulfate), concentrated, and chromatographed on silica gel. Elution with 1:1:10 (dichloromethane/ether/hexanes) gave 2,3-diphenyl-4-(trimethylsilyl)-benzoquinone **57** (23.4 mg, 27.1%; yellow solid, mp 89–90 °C, R_f = 0.65, 1:1:10) and 2,3-diphenylbenzoquinone **56** (17.1 mg, 25.3%; orange solid, mp 122–124 °C, R_f = 0.37, 1:1:10). Spectral data for the silyl quinone

Table V. Crystal Data for **55**

empirical formula	$C_{22}H_{24}O_2Si$
color; habit	red needle
crystal size (mm)	0.15 × 0.15 × 0.3
crystal system	monoclinic
space group	$P2_1/n$
unit-cell dimensions	a = 6.1680 (10) Å
	b = 19.302 (4) Å
	c = 16.877 (3) Å
	β = 96.98 (3)°
volume	1994.4 (6) Å^3
Z	4
formula weight	348.5
density (calcd)	1.161 mg/m^3
absorption coefficient	0.123 mm^{-1}
F(000)	744

Table VI. Data Collection for **55**

diffractometer used	Syntex $P2_1$
radiation	Mo Kα (λ = 0.71073 Å)
temperature (K)	298
monochromator	highly oriented graphite crystal
2θ range	0.0–40.0°
scan type	2θ–θ
scan speed	variable; 2.00–10.00 deg/min in 2θ
scan range (2θ)	2.00° plus Kα-separation
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
standard reflections	3 measured every 47 reflections
index ranges	$-5 \le h \le 5, 0 \le k \le 18, 0 \le l \le 16$
reflections collected	2183
independent reflections	1864 (R_{int} = 0.00%)
observed reflections	1323 ($F > 4.0\sigma(F)$)
absorption correction	N/A

(44) Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1480.
(45) Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390.
(46) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.
(47) We thank a reviewer for suggesting this possibility.
(48) Grevels, F. W.; Skibbe, V. *J. Chem. Soc., Chem. Commun.* **1984**, 681.

Table VII. Solution and Refinement for **55**

system used	Siemens SHELXTL PLUS (PC Version)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute structure	N/A
extinction correction	N/A
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
number of parameters refined	228
final R indices (obs data)	$R = 5.43\%$, $R_w = 6.07\%$
R indices (all data)	$R = 7.90\%$, $R_w = 6.59\%$
goodness-of-fit	1.45
largest and mean Δ/σ	0.002, 0.000
data-to-parameter ratio	5.8:1
largest difference peak	0.26 eÅ^{-3}
largest difference hole	−0.20 eÅ^{-3}

57: ^{1}H NMR (CDCl$_3$) δ 0.34 (s, 9 H), 7.34–7.42 (m, 11 H); ^{1}13C NMR (CDCl$_3$) δ −1.0, 128.5, 128.7, 129.1, 130.0, 130.1, 141.4, 149.7, 150.2, 152.0, 190.4, 192.4; IR (film) 3061 w, 2954 m, 1728 m, 1690 vs, 1631 w, 1486 w, 1443 w, 1352 m, 1246 m, 1122 s, 845 s, 692 s; mass spectrum, m/e (% relative intensity) 332 M$^+$ (90), 317 (100), 303 (10), 289 (20), 273 (8), 259 (10), 245 (12), 229 (15), 215 (45); calcd for $C_{21}H_{20}O_2Si$ m/e 332.1233, found m/e 332.1263. Spectral data for quinone **56**: ^{1}H NMR (CDCl$_3$) δ 6.93 (s, 2 H), 6.98 (dd, 4 H, J = 7.7, 1.7 Hz), 7.19–7.22 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ 127.7, 128.4, 130.4, 132.4, 136.4, 143.4, 187.0; IR (film) 3060 w, 2926 w, 1654 vs, 1443 w, 1326 w, 1296 m, 1090 m, 1010 m, 843 w, 744 m, 696 s; mass spectrum, m/e (% relative intensity) 260 M$^+$ (100), 231 (20), 215 (8), 202 (10), 178 (30), 152 (10); calcd for $C_{18}H_{12}O_2$ m/e 260.0837, found m/e 260.0858.

When the reaction was repeated but the oxidative workup was deleted, the cyclopentadienone **55** could be isolated from this reaction mixture and purified by chromatography on silica gel to give **55** as a dark-purple solid (mp 118–120 °C, R_f = 0.49, 1:1:4): ^{1}H NMR (CDCl$_3$) δ 0.15 (s, 9 H), 1.95 (s, 2 H), 4.10 (s, 3 H), 7.2–7.3 (m, 5 H), 7.34 (m, 5 H); ^{13}C NMR (CDCl$_3$) δ −0.35 (s, CH$_3$), 12.75 (t, CH$_2$), 59.61 (q, OCH$_3$), 126.55 (s), 127.99 (s), 128.67 (d), 128.77 (d), 129.24 (s), 130.32 (d), 130.50 (d), 131.44 (s), 132.39 (s), 148.32 (s, C-2), 168.53 (s, C-3), 200.48 (s, C-1); IR (CCl$_4$) 3084 w, 3059 m, 3022 w, 1730 m, 1708 s, 1693 s, 1648 s, 1617 m, 1485 w, 1447 w, 1406 w, 1349 m, 1314 m, 1293 s, 1179 w, 1163 w, 1144 w, 1123 w, 1078 w, 1047 w, 1029 w, 959 w, 904 w, 881 w cm^{-1}; mass spectrum, m/e (% relative intensity) 349 M$^+$ + 1 (4), 348 M$^+$ (19), 334 (11), 333 (46), 318 (6), 317 (21), 215 (6), 178 (3), 73 (100); calcd for $C_{22}H_{24}O_2Si$ m/e 348.1615, measured m/e 348.1550.

Crystal Structure of the ((Trimethylsilyl)methyl)cyclopentadienone 55. A single crystal of **55** suitable for X-ray analysis was grown from ethyl acetate/hexane. The approximate size of the crystal used for data collection measured 0.15 × 0.15 × 0.3 mm. The crystal was mounted on a Nicholet P2$_1$ automatic diffractometer equipped with an incident beam graphite crystal monochromator. All measurements were made at 25 °C using Mo Kα radiation. The unit-cell constants and the orientation matrix to be used in data collection were obtained from a least square refinement of 15 centered general reflections. Crystal data are listed in Table V. Table VI summarizes the data collection. No decay was noted for the three standard reflections. The solution and refinement is summarized in Table VII.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8821326). The National Institutes of Health has provided predoctoral training grants for C.A.C (GM 07183), K.L.F. (GM 07151), and D.C.Y. (GM 07151). The Organic Division of the American Chemical Society has provided a predoctoral fellowship to S.C. sponsored by the American Cyanamid Company. Some of the mass spectral data were obtained at the Midwest Center for Mass Spectrometry, an NSF Regional Instrument Facility (Grant CHE-8211164). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program.

Supplementary Material Available: X-ray crystallographic data for compound **55** including a figure showing the molecular structure and numbering scheme and tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (6 pages); a listing of observed and calculated structure factors for **55** (5 pages). Ordering information is given on any current masthead page.

Trifluoromethanesulfonyl Hypofluorite, a Hitherto Unknown Fluoroxy Compound

Evan H. Appelman* and Albert W. Jache

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439. *Received August 10, 1992*

Abstract: Trifluoromethanesulfonyl hypofluorite (CF_3SO_2OF) has been synthesized by the reaction of fluorosulfuryl hypofluorite (FSO_2OF) with cesium trifluoromethanesulfonate. It is the first compound in which a sulfur atom is bonded both to carbon and to an O–F moiety. The compound has a melting point of −87 ± 2 °C and an extrapolated boiling point of 0 ± 1 °C. The ^{19}F NMR spectrum of the compound in CFCl$_3$ at −80 °C shows a CF$_3$ doublet at −71 ppm and a broad OF singlet at +238 ppm. From the latter can be deduced an O–F bond energy of about 145 kJ/mol, comparable to that of FSO_2OF. The compound hydrolyses in base to give a mixture of O_2 and CF_4, along with (presumably) sulfate and trifluoromethanesulfonate. It decomposes thermally in the presence of CsF to yield principally CF_3SO_2F and OF_2 along with (presumably) cesium trifluoromethanesulfonate.

The successful synthesis in recent years of a variety of unexpected hypofluorites or fluoroxy compounds, i.e., compounds containing the O–F moiety, has effectively undermined most preconceptions as to which of these compounds might be synthesized. Nevertheless, a few islands of "nonexistence" have persisted, among which are compounds containing an S–O–F linkage and in which the sulfur is also bonded to carbon. We would expect formation of such a compound to be favored if the carbon were also surrounded by highly electronegative substituents. Nevertheless, the simplest compound that meets this criterion, trifluoromethanesulfonyl hypofluorite ("triflyl" hypofluorite, CF_3SO_2OF) has until now remained unknown. The conventional rationalization for its nonexistence has been the weakness of the carbon–sulfur bond, which would be readily susceptible to oxidative cleavage by the hypofluorite fluorine.

The two most general methods of synthesizing hypofluorites are the metal-fluoride-catalyzed addition of molecular fluorine across an M=O or M≡O multiple bond, as in the formation of

0002-7863/93/1515-1376$04.00/0